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THE JOURNAL

—OF THE—

AMERICAN CHEMICAL SOCIETY.

VOLUME XXI.

1899.

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JOHNSON REPRINT CORPORATION
NEW YORK, N. Y., U S. A.

PHOTOLITHOGRAPHED BY
THE MURRAY PRINTING COMPANY
WAKEFIELD, MASSACHUSETTS

PAPERS.

JANUARY.

FEBRUARY.

MARCH.

APRIL.

MAY.

JUNE.

JULY.

AUGUST.

SEPTEMBER.

OCTOBER.

NOVEMBER.

DECEMBER.

VOL. XXI. [JANUARY, 1899.]

THE JOURNAL

OF THE

AMERICAN CHEMICAL SOCIETY.

THE INVERSION OF SUGAR BY SALTS.

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Received September 20, 1898.

INTRODUCTION.

THE inversion of cane-sugar by salts has been studied by Walker and Aston[1], who determined the affinity of weak organic bases by ascertaining the extent to which their hydrochlorides are decomposed by water from the speed with which solutions of these salts invert sugar. They also measured the speed with which sugar is inverted by the nitrates of lead, cadmium, aluminum, zinc, and hydrogen. The work on the inorganic salts was conducted at 80°C., the sugar solution used being about ten per cent. The results are given in Table I, the coefficient C indicating the speed of the inversion.

TABLE. I.

Nitrates.	C.	Hydrolysis per cent. in equiv. $\frac{n}{9}$ solution.
Cadmium ($\frac{n}{9}$)	0.000154	0.014
Zinc ($\frac{n}{9}$)	0.000207	0.019
Lead ($\frac{n}{9}$)	0.001590	0.015
Aluminum ($\frac{n}{9}$)	0.007700	0.700
Hydrogen ($\frac{n}{1000}$)	0.002250	....

As the speed of inversion is proportional to the concentration of the hydrogen ions present (the latter being formed by the hydrolysis of the salt) the coefficients represent roughly the relative strengths of the respective bases. In the last column of

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[1] *J. Chem. Soc.*, London, 67, 576.

the table are the percentages of hydrolysis in equivalent half-normal solutions as deduced by comparing the values of C for the salts with that of the millinormal nitric acid solution.

J. H. Long[1] made a more extensive investigation of the inversion of sugar by inorganic salts. He pointed out that salts of the heavy metals in general have the power of inverting sugar solutions, and in some cases very rapidly, especially at an elevated temperature. He also correctly indicated that the cause of the inversion by these salts is to be found in their condition of partial hydrolysis by the solvent. Long gave special prominence to the work with ferrous salts; in addition to these, however, he investigated the chlorides of manganese, cadmium, mercury, and lead, the sulphates of manganese, zinc, and aluminum (potassium alum), and the nitrate of lead. The coefficients expressing the rate of inversion were calculated and the percentages of hydrolyzed salt were deduced by comparing these coefficients with that obtained by employing a millinormal hydrochloric acid solution under like conditions. The temperature at which Long's systematic investigations were performed is 85°, and the sugar solution used was of such strength that fifty grams were contained in 250 cc.

In the investigations of Walker and Aston and also in those of Long the polariscope was used exclusively to follow the progress of the inversion. This is no doubt the simplest and most accurate method to use whenever it is applicable. It is evident, however, that the polariscope cannot be used in working with colored solutions and that the accuracy of measurement with this instrument is greatly impaired when the solutions are not perfectly clear. Long cites several instances where, after prolonged heating, the solutions became somewhat colored or turbid, making their polarization difficult.

The objects of this investigation are: (1) to find a method by means of which the speed of inversion of sugar by colored salts can be determined, and (2) to compare the basicity of the metals as ascertained by the method of sugar inversion with their so-called solution tensions, as found by the measurement of the electromotive forces of galvanic chains.

The inversion of sugar is expressed by the equation:

$$C_{12}H_{22}O_{11} + H_2O = 2C_6H_{12}O_6.$$

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[1] This Journal, 18, 120 and 693.

If the solution is not too concentrated, the change in the number of molecules of water may practically be neglected. From the equation it appears that during the process of inversion each molecule of cane-sugar is converted into two molecules. Now since the osmotic pressure exerted by a dissolved substance is proportional to the number of its molecules, it is clear that when inversion is complete the dissolved sugar will exert just double the osmotic pressure that it did in form of cane-sugar. Furthermore, by measuring the osmotic pressure from time to time during the progress of the inversion, the rate of the latter may be determined. As the methods that are known at present for the direct measurement of the osmotic pressure could not be used advantageously, it was decided to measure some physical property that is proportional to the osmotic pressure. The lowering of the freezing-point and the elevation of the boiling-point suggested themselves. Trevor and Kortright[1] have shown that by noting from time to time the boiling-point of a sugar solution to which a small quantity of acid has been added, the speed of the inversion can be determined. A few preliminary tests indicated that the boiling-point method is not well suited for studying the inversion of sugar by salts of the heavy metals, for by boiling the solutions some of these salts suffer considerable reduction. The freezing-point method was consequently chosen, although less convenient of execution. Before this method was applied in the work with colored salts it was definitely ascertained that it would yield reliable results. This was done by following the progress of the inversion of several colorless solutions by both the polariscope and cryoscopic methods.

METHOD OF EXPERIMENTATION.

The following is an outline of the method of experimentation. The desired quantities of sugar and salt were weighed out and each was dissolved in a small quantity of water, generally with the aid of heat. These solutions were then thoroughly cooled and finally mixed in a graduated flask, cold water being added to fill the latter to the mark. It was found that at room temperature the inversion takes place very slowly; nevertheless no time was lost unnecessarily in transferring the solution to test-tubes, generally eight to ten in number, which were then tightly

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[1] *Ztschr. phys. Chem.*, 14, 149.

stoppered with rubber stoppers or closed by fusing the ends. These tubes were then kept at a higher temperature in a thermostat, the time of their introduction into the latter was noted, and then from time to time one was taken out and quickly immersed in a bath of melting ice to cool it rapidly and thus check the reaction. Its contents were then examined with the polariscope or freezing-point apparatus or both. A few tests showed that at 0° the inversion in the solutions used was so slow that no change could be detected for hours. It was consequently not necessary to investigate each tube at once, but several could thus be collected and their contents tested in rapid succession. While this is of no particular importance in working with the polariscope, with which determinations are so easily made, it is very advantageous in employing the freezing-point method, as it admits of making the determinations more rapidly and with a greater degree of accuracy relatively. It consumes time to prepare the freezing mixture properly and to find the freezing-point of pure water on the thermometer scale. The latter operation of course must be performed each time a series of observations is made, as the reading of a Beckmann's thermometer for a fixed temperature varies from time to time, partly because changes in the barometric pressure affect the bulb, and partly because minute amounts of mercury escape from the mercury that is attached to the thread in the upper chamber to the lower part of that chamber. The mercury can often be seen in form of very fine drops condensed on the sides of the upper chamber after the thermometer has stood for a number of hours.

Crystallized cutloaf sugar of a high degree of purity was used in all the experiments. It was dried, pulverized, and thoroughly mixed. For each series of experiments 84.93 grams were weighed out and dissolved in a small amount of water in a 500 cc. flask that was carefully graduated. The cold solution containing one-fourth of a gram equivalent of the salt to be investigated was then added. The solutions were mixed and finally made up to exactly 500 cc. Thus the resulting solution was half-normal with respect to each, the sugar and the salt.[1] All the salts used were of the C. P. variety of standard makes. They were recrystallized several times to free them from any

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[1] In a few cases less concentrated solutions had to be used on account of the slight solubility of the salt.

excess of acid they might contain. Thirty cc. of the solution last named were introduced into each of the test-tubes, which were twenty cm. long. These were then quickly sealed in a hot pointed flame. The liquid did not change its temperature materially during this operation. After the supply of twenty cm. test-tubes was exhausted, eighteen cm. ones were used; these could not be sealed as readily without heating the solution somewhat, so they were tightly stoppered with rubber stoppers.

The bath in which the tubes were placed is shown in Fig. 1. The cylindrical outer vessel *A* is thirty cm. high and thirty cm. in diameter. It is fitted with a similarly shaped inner vessel *B*, so that the distance between the sides of the two vessels is about four cm. and that between the bottoms eight cm. This part of the apparatus is made of tin. A spiral return condenser of glass is fitted to *A* as indicated. A bent glass tube *D* serves as a gauge to indicate the height of the liquid in *A*. *B* contains water in which the test-tubes are immersed. It has a wooden cover through which a thermometer is inserted. The test-tubes are held in position by wires as indicated. These wires are soldered on a disk of heavy tin provided further with a stout central wire *E*, by means of which all the tubes together with the supporting disk can be placed into the apparatus at the same time.

Fig. 1.

At first it was proposed to perform the experiments at about

80° C.; but a preliminary test on copper sulphate, using alcohol in the vessel *A*, showed that this temperature was too high inasmuch as partial reduction of the salt to the cuprous condition and even to metallic copper occurred. After still further tests, the temperature of boiling acetone, 55.5° C. was finally chosen.

The acetone was placed in *A* (Fig. 1), and kept boiling by a small flame. Water of the temperature of about 65° was poured into *B* to such a height that when the tubes were finally introduced they were sufficiently immersed! By introducing the cold tubes into this bath of a little higher temperature than finally desired, the temperature of the whole soon became 55.5°. This did not require more than three or four minutes. The tubes were ordinary test-tubes. They were cleaned with concentrated hydrochloric acid, washed with water, and finally thoroughly steamed according to Ostwald's[1] suggestion. A sample of the solution was always retained for making the initial determination. The time when the tubes were introduced into the bath was taken as the starting-point and placed equal to zero. This, of course, was not quite correct, as the temperature was not instantly adjusted. The error introduced was not great, however; it would show itself mainly in the first coefficient found, which would be a little too low.

The polariscope used was a triple field instrument manufactured by Schmidt & Haensch. It was of a pattern devised by Landolt.[2] All the observations were made in a twenty cm. tube at 20° C., the liquids being kept at this temperature during the time of the determination by running water of 20° C. through the jacket surrounding the observation tube.

The freezing-point apparatus was essentially of the form of that constructed by Beckmann,[3] but its dimensions were larger The tube containing the solution and the differential thermometer had no side neck; it was about twenty-two cm. long, and nearly five cm. in diameter. The thermometer and the stirrer[4] passed through the cork as usual, but the latter was further provided with another opening through which the freezing could be

[1] Hand- u. Hilfsbuch, p. 295.

[2] *Ber. d. chem. Ges.*, 28, 3102.

[3] Compare Ostwald's Hand- u. Hilfsbuch, p. 216.

[4] The stirrer had the usual shape, but was made entirely of glass. With an apparatus of the above dimensions this works very well and is much cheaper than the usual stirrer with the heavy platinum loop.

inaugurated by "vaccinating" the slightly overcooled liquid with a bit of ice. The air jacket was made of heavy tin; it was soldered to the cover of the jar, and the whole was then heavily coated with asphaltum to prevent rusting. The jar containing the freezing-mixture was an ordinary large size gravity battery jar. A Beckmann's thermometer was used. It was graduated to hundredths and the thousandths could be judged by means of a lens. Generally thirty cc. of the solution were tested. The temperature of the bath was so regulated that it was only a few tenths of a degree lower than the freezing-point of the liquid tested.

The calculation of the coefficient C expressing the speed of the reaction was made according to the well-known formula $C = \frac{1}{t} \log_{10} \frac{A}{A-x}$, in which A represents the amount of cane-sugar present at the beginning, and x the amount inverted during the time t. In working with the polariscope, A is measured by the total change in rotation observed from the beginning to the end of the reaction, and x is measured by the change in rotation during the time t. In applying the freezing-point method, A is measured by the total increase in the lowering of the freezing-point of the solution from the beginning to the end of the reaction, and x is measured by the increase in the lowering during the time t. In thus applying these methods, it is assumed that the influence of the salt present in solution on the rotation and freezing-points respectively is constant throughout the reaction. Though the action of the salt on the cane-sugar, and the invert sugar is probably slight, some interaction does seem to take place as Long[1] has already pointed out.

A half-normal solution of cane-sugar gave as an average of four series of independent experiments a lowering of the freezing-point of 1.114°. A solution that was half-normal with respect to cane-sugar, and centinormal with respect to hydrochloric acid gave a lowering of 2.248° after complete inversion had taken place. The sugar after inversion would theoretically cause the lowering to be 2.228°, consequently the difference, 0.020°, is the lowering caused by the acid. Theoretically the hydrochloric acid ought to give the lowering 0.019°; but since in centinormal

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[1] This Journal, 18, 716.

solution the dissociation is nearly complete, this figure would become 0.038°. It is clear then that the above result, 2.248°, is a little too low, theoretically considered; it was thought to be sufficient, however, to warrant adopting the figure 1.114° in future calculations as the increase of lowering of the freezing-point caused when the inversion is complete.

It is somewhat difficult at times to obtain the exact rotation of the plane of polarization of a sugar solution after complete inversion because of changes produced by prolonged heating.[1] For this reason, the calculated value found by reckoning 0.315°[2] negative rotation for every degree of initial positive rotation was used as the end-point of the reaction except when the observed value exceeded it. Thus, the most probable initial angle for the twenty cm. tube was found to be 22.60°; the end-point would consequently be 22.60° × —0.315 or —7.12°.

RESULTS.

The experimental results will now follow in detail.

TABLE II.

Hydrochloric Acid.

In 1000 cc., ½ g. mol. $C_{12}H_{22}O_{11}$ plus $\frac{1}{100}$ g. mol. HCl. (Polariscope.)

Time, hours.	Rotation.	Change.	C.
0.0	22.62°	.....	......
1.0	16.58	6.04	0.0983
2.0	9.92	12.70	0.1205
2.5	7.68	14.94	0.1208
3.0	5.94	16.68	0.1186
4.0	2.54	20.08	0.1215
4.5	1.42	21.20	0.1198
7.0	—2.40	25.02	0.1130
17.5	—6.90	29.52	0.1142
26.5	—7.20	29.82	......
			0.1158

TABLE III.

Hydrochloric Acid.

In 1000 cc., ½ g. mol. $C_{12}H_{22}O_{11}$ plus $\frac{1}{100}$ g. mol. HCl. (Freezing-point.)

Time, hours.	Lowering.	Change.	C.
0.0	1.175°	.....	......
1.0	1.393	0.218	0.0977
2.0	1.635	0.460	0.1217
2.5	1.705	0.530	0.1185
3.0	1.809	0.634	0.1296
4.0	1.912	0.737	0.1263
4.5	1.954	0.779	0.1252
7.0	2.105	0.930	0.1254
17.5	2.230	1.055	0.1028
26.5	2.247	1.072	......
			0.1147

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[1] Compare Long: This Journal, 18, 697.

[2] Compare Rayman and Sulc: *Ztschr. phys. Chem.*, 21, 488.

In Table II, —7.2° was taken as the end-point and in Table III, 2.247°, for the change that had taken place in nine hours was but 0.3° on the polariscope scale and 0.017° on that of the thermometer. Considering the experimental difficulties encountered in the work the agreement of the values of C in Table III, with those in Table II, must be considered sufficient. It has been established therefore that the freezing-point method can be successfully used to determine the rate of inversion of sugar. As the amount of hydrochloric acid present was small as compared with the amount of sugar, this was an especially favorable case in which to test the reliability of the cryoscopic method in following the progress of the reaction. Further comparisons between the two methods in which salts were used to invert the sugar will be given below.

ALUMINUM SALTS.

The aluminum salts investigated are potassium alum, aluminum sulphate and chloride. The alum solution was weaker than the usual strength on account of the low solubility of the salt in the cold.

TABLE IV.

Potassium Alum.

In 1000 cc., ¼ g. mol. $C_{12}H_{22}O_{11}$ plus $\frac{1}{32}$ g. mol. $K_2Al_2(SO_4)_4$. (Polariscope.)

Time, hours.	Rotation.	Change.	C.
0.0	11.23°	....	....
1.0	10.48	0.75°	0.02260°
2.0	9.29	1.94	0.03053
4.0	8.12	3.11	0.02551
6.5	6.35	4.88	0.02675
8.0	5.54	5.69	0.02637
41.25	—2.54	13.77	0.02815
83.5	—3.16	14.39	0.02525
∞	—3.56	14.79	....
			0.02645

TABLE V.

Potassium Alum.

In 1000 cc., ¼ g. mol. $C_{12}H_{22}O_{11}$ plus $\frac{1}{32}$ g. mol. $K_2Al_2(SO_4)_4$. (Freezing-point.)

Time, hours.	Lowering.	Change.	C.
0.0	0.855°	....	....
1.0	0.859(?)	0.004°(?)	0.00313°(?)
2.0	0.889	0.034	0.01368
4.0	0.925	0.070	0.01458
6.5	0.980	0.125	0.01697
8.0	1.009	0.144	0.01757
41.25	1.278	0.423	0.01502
83.5	1.327	0.472	0.01002
∞	1.412	0.557	....
			0.01464

Tables IV and V show that alum inverts sugar rapidly.[1] The values of C in Table V, are only about half as large as those in Table IV. It seems that a change decreasing the number of molecules in the solution must be going on in this case as time elapses; the matter was not studied further, but it deserves investigation. The value of C in Table IV is the more reliable one. The inversion in case of the alum solution is caused by the aluminum sulphate present, which is hydrolyzed. It is a well-known fact that a solution obtained by mixing potassium sulphate and aluminum sulphate in molecular proportions, is the same as an equivalent solution of alum. Table VI shows that the potassium sulphate is not the cause of the inversion, and Table VII clearly shows that the aluminum sulphate is the active agent.

TABLE VI.

Potassium Sulphate.

In 1000 cc., ½ g. mol. $C_{12}H_{22}O_{11}$ plus ½ g. mol. K_2SO_4. (Polariscope.)

Time, hours.	Rotation.	Change.
0.0	22.54	....
3.0	22.40	0.14
16.5	22.06	0.46
25.0	22.22	0.32

TABLE VII.

Aluminum Sulphate.

In 1000 cc., ½ g. mol. $C_{12}H_{22}O_{11}$ plus $\frac{1}{12}$ g. mol. $Al_2(SO_4)_3$. (Polariscope.)

Time. hours.	Rotation.	Change.	C.
0.0	22.54°	....	......
3.5	16.39	6.15	0.02884
6.0	12.32	10.22	0.03058
8.0	9.91	12.63	0.03012
10.0	7.26	15.28	0.03244
14.0	4.14	18.40	0.03006
21.0	—0.26	22.80	0.03028
24.0	—1.64	24.18	0.03055
29.0	—3.10	25.64	0.02993
37.0	—4.82	27.36	0.03001
55.0	—6.44	28.98	0.02980
∞	—7.12	29.66	......
			0.03026

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[1] The same was found by Long: *l. c.*

Table VII shows that the aluminum sulphate solution inverts very rapidly, a little over one-fourth as rapidly as does centinormal hydrochloric acid (Tables II and III). As the solution used in Table VII is not equivalent to that in Table IV, the constants are not directly comparable. We should expect alum to invert less rapidly, however, than an equivalent amount of aluminum sulphate, for the presence of the potassium sulphate tends to decrease the number of hydrogen ions in the solution.[1]

TABLE VIII.

Aluminum Chloride.

In 1000 cc., ½ g. mol. $C_{12}H_{22}O_{11}$ plus ⅙ g. mol. $AlCl_3$. (Polariscope.)

Time, hours.	Rotation.	Change.	C.
0	22.47°	....	......
6	6.92	15.55	0.0539
18	—1.98	24.45	0.0366
25	—4.44	26.91	0.0417
45	—6.45	28.92	0.0365
∞	—7.13	29.59	......
			0.0422

The chloride was of Schuchardt's make. It was recrystallized three times. A comparison of Tables VII and VIII shows that the chloride inverts much faster than the sulphate. This is what one would be inclined to expect from the strong ionizing tendency of chlorine. (This point will come up again below.) Long found that ferrous chloride inverts much more rapidly than ferrous sulphate.

MANGANESE SALTS.

TABLE IX.

Manganous Sulphate.

In 1000 cc., ½ g. mol. $C_{12}H_{22}O_{11}$ plus ¼ g. mol. $MnSO_4$. (Polariscope.)

Time, hours.	Rotation.
0	21.64°
5	22.12
10	22.20
15	22.34
20	22.10
25	22.50
35	22.14

---

[1] Long found that ferrous sulphate inverts faster than ferrous ammonium sulphate, which illustrates the same point

Table IX shows that manganous sulphate does not invert sugar appreciably at 55.5° C. The readings obtained vary irregularly within the limits of experimental error. At higher temperatures this salt does invert sugar, but of course very slowly (compare Long : *l. c.*).

TABLE X.

Manganous Chloride.

In 1000 cc., ¼ g. mol. $C_{12}H_{22}O_{11}$ plus ¼ g. mol. $MnCl_2$. (Polariscope.)

Time, hours.	Rotation.	Change.	C.
0.0	22.79°	....	....
5.5	22.72	0.07	0.000185
12.0	22.65	0.14	0.000170
24.0	22.54	0.25	0.000152
36.0	22.45	0.34	0.000138
48.0	22.23	0.56	0.000171
300 (about)	21.92	0.87	....
∞	—7.12	29.91	....
			0.000163

Table X shows that manganous chloride does invert slightly. Here again we see that the chloride inverts faster than the sulphate. In working at 80° C., Long also found that manganous chloride inverts much more rapidly than does the sulphate.

ZINC SALTS.

Of the zinc salts only the sulphate was tested. The specimen was a particularly fine one. Table XI shows that the inversion caused by this salt at 55.5° is very slight, but little change having taken place in fifty hours.

TABLE XI.

Zinc Sulphate.

In 1000 cc., ¼ g. mol. $C_{12}H_{22}O_{11}$ plus ¼ g. mol. $ZnSO_4$. (Polariscope.)

Time, hours.	Rotation.
0.0	22.52°
2.0	22.38
6.0	22.38
20.66	22.42
46.0	22.02
50.0	21.96

The same solution heated in a water-bath to 100° C. gave the results in Table XII.

TABLE XII.

Zinc Sulphate.

In 1000 cc., ½ g. mol. $C_{12}H_{22}O_{11}$ plus ¼ g. mol. $ZnSO_4$. (Polariscope.)

Time, hours.	Rotation.	Change.	C.
0.0	21.96°	....	......
1.0	18.84	3.12	0.04929
2.0	15.00	6.96	0.05940
3.0	12.22	9.74	0.05904
4.5	3.84	18.12	0.09417
8.16	−3.50	25.46	0.11089
∞	−7.12	29.08	......

After three to four hours' heating the solution became colored. An acid odor was also perceptible. After three hours the values of C ran up rapidly. Long also noted an increase in the value of the coefficient at 80° C.

CADMIUM SALTS.

Cadmium sulphate inverts very slowly indeed as both the polariscopic and cryoscopic tests show (Table XIII). The inversion is practically nil.

TABLE XIII.

Cadmium Sulphate.

In 1000 cc., ½ g. mol. $C_{12}H_{22}O_{11}$ plus ¼ g. mol. $CdSO_4$. (Polariscope.)

Time, hours.	Rotation.	Freezing-point lowering.
0.0	22.23°	1.720°
5	22.49	1.756
10	22.72	1.745
15	22.58	1.747
19	22.54	1.754
24	22.75	1.758
34	22.65	1.755
44	22.72	1.754

Cadmium chloride was tested and gave similar results, as Table 14 shows. This salt was particularly pure.

TABLE XIV.

Cadmium Chloride.

In 1000 cc., ½ g. mol. $C_{12}H_{22}O_{11}$ plus ¼ g. mol. $CdCl_2$. (Polariscope.)

Time, hours.	Rotation.
0.0	22.30°
2.0	22.54
3.0	22.62
8.0	22.62
5.0	22.60
18.0	22.28
26.0	22.46
46.25	....

Another fine-looking sample of cadmium chloride of Schuchardt's manufacture was tested by both the polariscope and freezing-point methods. This salt, which was not recrystallized, yielded the results in Tables XV and XVI.

TABLE XV.

Cadmium Chloride.

In 1000 cc., ½ g. mol. $C_{12}H_{22}O_{11}$ plus ¼ g. mol. $CdCl_2$. (Polariscope.)

Time, hours.	Rotation	Change.	C.
0.0	21.63°	....	......
3	7.57(?)	13.06	0.08375
16	5.94	15.69	0.05430
10	—0.28	21.91	0.05793
15	—3.82	25.45	0.05612
20	—5.71	27.34	0.05474
25	—6.90	28.53	0.05576
35	—7.70	29.33	0.05346
∞	....	29.73	......

TABLE XVI.

Cadmium Chloride.

In 1000 cc., ½ g. mol. $C_{12}H_{22}O_{11}$ plus ¼ g. mol. $CdCl_2$. (Freezing-point.)

Time, hours.	Lowering	Change.	C
0	2.872°	....	......
3	2.176(?)	....	......
6	3.584	0.712	0.07389
10	3.700	0.828	0.05916
15	3.836	0.964	0.05822
20	3.919	1.047	0.06134
25	3.960	1.098	0.07480
35	3.977	1.105	0.08390
∞	3.986	1.114	......

The values of C in Table XVI are somewhat higher and more irregular than those of Table XV. This is to be ascribed to the difficulty in working with such strong solutions by the freezing-point method. The values of C in both tables seemed abnormally high, however, and consequently the salt was recrystallized twice and then tested again, this time with the polariscope only. Table XVII gives the results found.

TABLE XVII.

Cadmium Chloride.

In 1000 cc., ½ g. mol. $C_{12}H_{22}O_{11}$ plus ¼ g. mol. $CdCl_2$. (Polariscope.)

Time. hours.	Rotation.	Change.	C.
0	22.60°	....	......
4	22.12	0.48	0.00177
20	20.85	1.75	0.00132
30	20.28	2.32	0.00121
45	19.61	2.99	0.00102
70	18.75	3.85	0.00086
100	17.88	4.72	0.00075
∞	—7.13	29.73	......

The values of C in Table XVII continually decrease. They are much smaller than those in Tables XV and XVI, which shows that recrystallization further purified the salt by removing free acid that probably adhered to it. Long found a relatively very high coefficient for this salt at 80° C. He states that the salt he used was recrystallized several times, and was free from uncombined acid. As the above work shows that pure cadmium chloride inverts exceedingly slowly at 55.5° C., the inference must be drawn that the rate of inversion of sugar by this salt increases rapidly as the temperature rises. To test this inference, the same salt as was used to obtain the results in Table XIV was investigated at 100° C. Table XVIII gives the results obtained, which show that the inversion does increase enormously with the temperature.

TABLE XVIII.

Cadmium Chloride.

In 1000 cc., ¼ g. mol. $C_{12}H_{22}O_{11}$ plus ½ g. mol. $CdCl_2$. (Polariscope.)

Time, hours.	Rotation.	Change.	C.
0.0	22.54°	....	......
1.0	11.16	11.38	0.21011
1.5	7.48	15.06	0.20511
2.0	3.82	18.72	0.21645
2.5	1.30	21.24	0.21859
3.0	—0.46	23.00	0.21606
4.5	—4.80	27.34	0.24554
7.0	—6.42	28.96	0.23158
∞	—7.13	29.67	......
			0.22049

NICKEL SALTS.

Only one salt of nickel, the sulphate, was tested. The salt was a very pure specimen; it was recrystallized several times to free it from any excess of acid. The results in Table XIX show that the salt inverts slowly. The reaction progresses very slowly after about ten hours.

TABLE XIX.

Nickel Sulphate.

In 1000 cc., ½ g. mol. $C_{12}H_{22}O_{11}$ plus ¼ g. mol. $NiSO_4$. (Freezing-point.)

Time, hours.	Lowering.	Change.	C.
0	1.713°	....	......
1	1.728	0.015	0.00589
2.5	1.731	0.018	0.00283
4.5	1.740	0.027	0.00237
9.75	1.772	0.059	0.00243
38.5	1.765	0.052	0.00054
∞	2.827	1.114	......

COPPER SALTS.

The rate of inversion by both the sulphate and chloride of copper was determined by means of the freezing-point method. Both salts were very fine samples. The sulphate was recrystallized three times and the chloride twice. In Table XX, the values of C gradually diminish to the sixteenth hour after which they increase. This increase is due to a reduction which the salt suffers after prolonged heating even at 55.5°. The last tube taken from the bath contained a deposit of metallic copper. This explains the high value of the final coefficient C.

TABLE XX.

Copper Sulphate.

In 1000 cc., ½ g. mol. $C_{12}H_{22}O_{11}$ plus ¼ g. mol. $CuSO_4$. (Polariscope.)

Time, hours.	Lowering.	Change.	C.
0	1.690°	....	......
1.25	1.721	0.031	0.00973
3.25	1.744	0.054	0.00661
5.25	1.754	0.064	0.00489
8.25	1.770	0.080	0.00392
12.25	1.795	0.105	0.00351
16.25	1.860	0.170	0.00442
28.75	2.407	0.717	0.15586
∞	2.804	1.114	......

TABLE XXI.

Copper Chloride.

In 1000 cc., ½ g. mol. $C_{12}H_{22}O_{11}$ plus ¼ g. mol. $CuSO_4$. (Freezing-point.)

Time. hours.	Lowering.	Change.	C.
0	2.446°	....	......
2	2.452	0.006	0.00118
5	2.484	0.038	0.00302
8	2.525	0.079	0.00400
12	2.595	0.149	0.00520
17	2.721	0.275	0.00726
23	2.836	0.390	0.00816
29	2.980	0.534	0.00980
45	3.365	0.919	0.01690
65	3.560	0.114	......
∞	3.560	0.114	......

In Table XXI, the values of C continually increase. This may be due to a reduction of the salt; the solution, however, remained clear from beginning to end. The inversion is complete in sixty-five hours. Comparing this table with the preceding one, it appears that the chloride inverts more slowly than the sulphate for about the first eight hours; after that, the former inverts much more rapidly. The final value of the coefficient in Table XX is, of course, abnormally high for the reason already mentioned.

MERCURY SALTS.

Of these salts only mercuric chloride was studied. The specimen used was a sublimed product. It was not recrystallized from water. Both the polariscopic and cryoscopic methods were used. The solutions became somewhat turbid toward the latter part of the reaction, probably because of a slight reduction of the salt to mercurous chloride, which separated out. This necessitated filtration of the solutions before they could be tested with the polariscope.

TABLE XXII.

Mercuric Chloride.

In 1000 cc., ½ g. mol. $C_{12}H_{22}O_{11}$ plus ¼ g. mol. $HgCl_2$. (Polariscope.)

Time, hours.	Rotation.	Change.	C.
0	22.59°	....	......
0.5	22.38	0.21	0.00616
2	21.88	0.71	0.00525
4	21.20	1.39	0.00520
7	20.19	2.40	0.00522
12	18.57	4.02	0.00526
17	16.11	6.48	0.00628
22	14.13	8.46	0.00661
∞	—7.12	29.71	......
			0.00572

TABLE XXIII.

Mercuric Chloride.

In 1000 cc., ½ g. mol. $C_{12}H_{22}O_{11}$ plus ⅛ g. mol. $HgCl_2$. (Freezing-point.)

Time, hours.	Lowering.	Change.	C.
0	1.293°	....	......
0.5	1.295	0.002	0.00158
2	1.323	0.030	0.00593
4	1.338	0.045	0.00448
7	1.376	0.083	0.00481
12	1.432	0.139	0.00482
17	1.519	0.226	0.00579
22	1.603	0.310	0.00644
32	1.674	0.381	0.00568
∞	2.407	1.114	......
			0.00542

The first coefficient in Table XXIII is very low. The experimental error in this case is, of course, relatively very great, since the increase of the lowering in half an hour is so small. No reliance whatever can be put on this first coefficient, and it has not been taken into consideration in the average. A comparison of the coefficients of Tables XXII and XXIII shows again the usefulness of the cryoscopic method in tracing the process of inversion, in spite of the many difficulties that are met in applying the method.

FERRIC SALTS.

Ferric potassium alum and ferric ammonium alum were tested, but the salts soon suffered reduction. A precipitate formed in these solutions in less than an hour and continued to increase rapidly. The sugar was speedily inverted as a few freezing-point tests showed.

AMMONIUM SALTS.

The effect of ammonium sulphate was studied at 55.5° and at 100°. No appreciable inversion took place at either temperature, although the mixture was kept at 55.5° for about sixty-seven hours. At 100° the solution turned brown after five hours' heating and, as it was being investigated with the polariscope, no more readings were made after that time. Ammonium chloride was tested only at the lower temperature. The readings showed that after heating for eighty hours a change of only 0.1° in rotation had taken place. Even this might have been error of observation.

In Table XXIV are collected the coefficients of inversion at 55.5° C. for solutions that are half-normal with respect to sugar and half-normal (equivalent) with respect to the salt. Those marked with an asterisk (*) are only rough averages, since the coefficients in the series are not constant. In the last column is given the degree of hydrolysis deduced by comparing the speed of inversion of the salt with that of centinormal hydrochloric acid under the same conditions. The comparison is only very rough at best.

TABLE XXIV.

Salt.	C.	Hydrolysis per cent. in equivalent half-normal solution.
Aluminum sulphate	0.03026	0.52
Aluminum chloride	0.0422	0.73
Manganese sulphate	....	....
Manganese chloride	0.00016	0.003
Zinc sulphate	....	....
Cadmium sulphate	....	....
Cadmium chloride	0.0014*	0.024
Nickel sulphate	0.00281*	0.048
Copper sulphate	0.00551*	0.095
Copper chloride	0.00694*	0.12
Mercuric chloride ($\frac{n}{2}$)	0.00572	0.2
Hydrogen chloride ($\frac{n}{100}$)	0.1158	....

Theoretical Considerations.

The hydrolytic decomposition of a salt may be expressed by the general equation:

$$MA + H_2O = MOH + HA,$$

in which M represents the metal and A the acid radical. If the metal has several valences, correspondingly more molecules of water enter into the reaction. The more dilute the solution is, the greater is the extent of the hydrolysis. If for the sake of simplicity we assume the solution to be so dilute that the electrolytic dissociation of the salt is practically complete, the reaction takes the form:

$$\overset{+}{M}, \overset{-}{A} + H_2O = MOH + \overset{+}{H}, \overset{-}{A}.$$

From this it appears that A remains in the ionic condition throughout. There must, of course, be present an equal number of cations in order to preserve the electrical neutrality of the solution. These cations are mainly those of the metal (if the salt is but slightly hydrolyzed), but there are also present hydrogen ions formed as indicated by the equation. The compound MOH, the hydroxide of the metal, is probably held in solution in colloidal form, in which case its molecules are polymerized. In stronger solutions this hydroxide may unite with undissociated molecules of the salt to form a basic compoud, which would gradually be broken upon further dilution. In general then at any stage of dilution a solution of a salt of a heavy metal contains (1) a certain number of undissociated molecules of the salt, (2) the anions of the electrolytically dissociated molecules, (3) ions of the metal plus hydrogen ions together chemically equivalent to the anions, (4) molecules of colloidal hydroxide of the metal or of a basic salt equivalent to the hydrogen ions. At each stage of dilution an equilibrium between these various classes of molecules establishes itself.

The acid radical A becoming ionized, forces positive ions to form. If the metal is such that it readily passes into the ionic condition (*e. g.*, the alkalies and alkaline earths), practically the only positive ions in the solution are those of the metal, and the solution has a neutral reaction and does not invert sugar; but if the metal assumes the ionic state less readily (*e. g.*, the heavy metals), the ions of the metal form up to a certain extent only, the rest of the necessary positive ions being supplied by the water, which is decomposed, yielding hydrogen ions and an hydroxyl residue that forms either a colloidal hydroxide of the metal or a basic salt, as already pointed out. It is clear that if the metal readily enters into such colloidal or basic combinations the formation of hydrogen ions will be aided thereby. In a solution of a ferric salt, the deepening of the color on further dilution indicates the presence of the colloidal hydroxide or very basic salt, whereas the acid reaction, the high electrical conductivity, the power to invert sugar, etc., indicate the presence of hydrogen ions. In solutions of other salts, the presence of the colloidal or basic compound is generally not as readily detected, either because it is less abundant or because it is colorless, and hence is less easily discovered. Colloidal hydroxides of some of the metals are well known, of others such substances are not known; but nearly all of the heavy metals form basic salts with more or less readiness. In most solutions the amount of such colloidal or basic compounds is small, the hydrolysis generally being less than one per cent. and but seldom exceeding three per cent.

For equivalent strengths of solutions the relative extent of the hydrolysis of salts of the same anion is determined by the readiness with which the various metals pass into the ionic state and the ease with which they form basic or colloidal compounds. The tendency that the metals have to pass from the metallic to the ionic condition is expressed by the so-called electrolytic solution tensions of the metals. These have been calculated from the differences of potential existing between the metals and normal solutions of their salts.[1] Since the passing of a metal from the metallic to the ionic state is not identical with the formation of cations from a salt after the latter is once formed, we should not expect to find a simple relation between the solution tensions of the metals and the degree to which their salts are hydrolyzed. Leaving out of consideration the tendency of the metal to enter colloidal or basic combinations, it might be expected, however, that the order in which the salts of the heavy metals of the same anion invert sugar be the same as that in the table of their solution tensions. This is in general found to be the case. According to Neumann[2] the order of the metals in the table of their solution tensions is: Aluminum, manganese, zinc, cadmium, iron, nickel, lead, copper, mercury.[3] Taking the results of Walker and Aston as given above and arranging the metals in the order in which their nitrates invert sugar, beginning with the one causing least inversion, we have: Cadmium, zinc, lead, aluminum. Here aluminum is last instead of first, and the order of cadmium and zinc is the reverse of that in the electrochemical series given above. A consideration of Long's results gives the order: Manganese, zinc, iron, aluminum for the sulfates, and manganese, iron, lead,[4] cadmium for

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[1] Compare Neumann: *Ztschr. phys. Chem.*, 14, 223 and 229; also LeBlanc's Elektrochemie, pp. 183 and 185.

[2] *Loc. cit.*

[3] Only those metals whose salts have been investigated as to their sugar-inverting power are here given.

[4] Taken from the nitrate.

the chlorides. According to the present investigation the order for the sulphates is: Nickel, copper, aluminum, the sulphates of manganese, zinc and cadmium having caused practically no inversion at 55.5°. The order for the chlorides is: Manganese, cadmium, copper, mercury, aluminum. While it is apparent that the order is, in general, similar to that in the electrochemical series, it is clear that aluminum is a striking exception, its salts being the most hydrolyzed of those tested instead of the least. According to Walker and Aston and also according to Long, the position of cadmium is lower in the series than it should be. The present work indicates that the inversion by cadmium chloride is especially influenced by temperature, and as the electrochemical series was determined at room temperature and the inversion was carried out at high temperatures, this might account for the abnormal position of cadmium. It remains to consider the relatively high degree of hydrolysis of aluminum salts. This metal, like iron in the ferric state, forms a colloidal hydroxide. According to the above considerations, this tendency of aluminum would aid the hydrolytic decomposition of its salts. The freezing-point results on alum solutions, indicating that a diminution of the number of molecules in solution occurs, deserves further study in this connection.

The results of Long, and also those contained in the foregoing tables, show that chlorides invert faster than sulphates. The explanation lies in the fact that chlorine has a greater tendency to pass into the ionic state than has SO_4. Hence in the solutions of the chlorides the number of anions is relatively greater and consequently the number of cations is also greater, resulting in an increase of the number of hydrogen ions and consequently more rapid inversion.

Summary.

The main results of this investigation may be summed up briefly as follows:

1. The freezing-point method may be successfully employed in determining the speed of the inversion of sugar.

2. When the metals are arranged in a series according to the speed with which their salts of the same acid radical invert sugar, it appears that the order is similar to that of the electro-

chemical series. Aluminum forms a notable exception. In spite of the high position of this metal in the electrochemical series, its salts invert sugar more rapidly than those of any other metal thus far tested.

3. Chlorides invert sugar more rapidly than sulphates, because the ionizing tendency of chlorine is greater than that of the sulphuric radical.

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE CASE SCHOOL OF APPLIED SCIENCE, NO. 32.]

SODIUM ALUMINATE AS A MEANS FOR THE REMOVAL OF LIME AND SUSPENDED MATTER FROM WATER FOR USE IN BOILERS.[1]

BY CHARLES F. MABERY AND EDWIN B. BALTZLEY.

Received October 5, 1898.

THROUGHOUT the section of country including Northern Pennsylvania, Ohio, and farther west, in districts removed from the lake or the large rivers, the only sources of water in seasons of drought are deep wells. Since the water from these wells contains large quantities of lime salts, there are serious difficulties in the way of procuring water suitable for use in steam boilers, especially in locomotive boilers. Even such water as that from Lake Erie or the rivers, deposit scale to such an extent as to occasion extreme inconvenience. In stationary boilers, the deposition of scale may be avoided at least in part by using some one of the many so-called scale preventatives, if the boiler is in charge of an intelligent engineer.

The inconvenience of boiler scale, the additional cost in fuel, the injury to the boiler, and the danger are features of this question familiar to all who have charge of boilers. The large masses of scale withdrawn from boilers in which hard or turbid water is used, are not surprising when the great quantities of water evaporated in boilers under high pressures are taken into consideration.

The wide variations in the composition of boiler scale are de-

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[1] The work described in this paper formed the subject of a thesis for the degree of Bachelor of Science.

pendent on the differences in the water used. The manner of running the boiler has much to do with the hardness of the scale and the rapidity of its formation. The chief causes of the formation of scale are the calcium carbonate and sulphate and magnesium carbonate contained in solution, and the solid matter held in suspension, both inorganic and organic. All these points must be borne in mind if unpurified water is to be used in a boiler. There has been for some time a feeling on the part of engineers that the only satisfactory method for the prevention of boiler scale is the use of purified water, and many attempts have been made, with more or less success, toward purification of the water before it enters the boiler. The means that have been tried include sedimentation, precipitation by sodium carbonate, sodium hydroxide, slaked lime either alone or in combination. Evidently successful purification depends on removing completely the suspended matter as well as the precipitation of the lime and magnesia. In thinking of what combination should most effectually and economically accomplish these results, in any hard or turbid water, it occurred to one of us (Mabery), that sodium aluminate should fulfill the conditions demanded, and in trying this reagent we find that it meets all requirements.

The general method includes the preparation of sodium aluminate in solution. This may be done in any suitable tank or reservoir, by adding sodium hydroxide in the proper amount to a solution of aluminum sulphate of known strength, and adding to the water a definite amount (the quantity depending on the composition of the water to be purified), agitating thoroughly, and allowing the mixture to stand some time, perhaps twelve to twenty-four hours. The method is based on the following reactions:

For the formation of sodium aluminate:

$$Al_2(SO_4)_3 + 8NaOH = Al_2O_4Na_2 + 3Na_2SO_4 + 4H_2O.$$

In the precipitation:

$$CaH_2(CO_3)_2 + Al_2O_4Na_2 + 2H_2O = CaCO_3 + 2AlO_3H_3 + Na_2CO_3.$$

$$CaSO_4 + Na_2CO_3 = CaCO_3 + Na_2SO_4.$$

Similar reactions evidently take place with magnesium carbonate or sulphate. No doubt sodium aluminate can be made much more cheaply by fusing a tolerably pure clay with soda-ash. Doubtless it may also be obtained cheaply as one of the products in the preparation of soda-ash from cryolite.

Numerous experiments were made with different proportions of sodium aluminate; the best results were obtained by using from one-half the calculated proportions to the calculated proportions of aluminum sulphate, depending on the composition of the water. With proper proportions of aluminate, aluminum hydroxide was completely precipitated on standing. Experiments on different waters with one-fourth the calculated proportion of aluminate showed that this amount was not sufficient to precipitate the lime sufficiently. In applying this method its effect was studied on waters containing different amounts of carbonate and sulphate, as well as on waters with a great variation in turbidity, from the slightly turbid lake water, to specimens thick and muddy. In every instance after standing from twelve to twenty-four hours, the water became perfectly clear. The extent to which lime and magnesia were removed is shown by results obtained in the following waters:

Very hard water from well in Ohio:

Calcium sulphate	259.0
Calcium carbonate	146.0
Magnesium carbonate	177.3

About eighty-five per cent. of the amount of aluminate required to precipitate all the lime and magnesia was added, air was blown through the solution for a few minutes and the mixture allowed to stand twenty-four hours. Analysis then showed that eighty-eight per cent. of the lime had been removed and 95.6 per cent. of the magnesia. In another determination the theoretical amount of aluminate was added and the solution treated as before. Analysis showed that 98.1 per cent. of the lime had been removed and 97.4 per cent. of the magnesia.

The next water tried was the Massillon city water, containing

Calcium sulphate	99.12
Calcium carbonate	113.2
Magnesium carbonate	131.1

After treatment with the theoretical amount of sodium aluminate the total lime removed was equivalent to 98.8 per cent., and that of magnesia 98.0 per cent.

In another experiment, using one-half the theoretical amount, the lime removed was 83.5 per cent., and that of the magnesia 90.6 per cent.

The next water tried was a very turbid sample from the Cuyahoga river. This water was very muddy and did not settle on long standing. It is used in boilers. A clear sample of this water showed the following composition :

Calcium sulphate	68.0
Calcium carbonate	14.14
Magnesium carbonate	21.3

Treatment with the theoretical amount of aluminate gave unsatisfactory results.

With twice the theoretical amount, the lime remaining was 88.3 per cent., and the magnesia 84.5 per cent. The aluminate is especially serviceable in such waters as this in removing completely the turbidity.

Although the water of Lake Erie does not contain a large proportion of solid matter, it forms scale quite rapidly unless some means are taken to prevent it. Analysis of a sample collected April 28, 1898, gave:

Calcium carbonate	53.63
Calcium sulphate	32.61
Magnesium carbonate	21.53

Analysis, after treatment with theoretical aluminate, gave 97.6 per cent. lime, and 93.2 per cent. magnesia removed, after standing thirty-six hours. With one-half the theoretical amount standing forty-eight hours 98.3 per cent. of the lime was removed and ninety per cent. of the magnesia. With one-fourth the theoretical amount eighty-three per cent. of lime was removed and sixty per cent. of the magnesia.

From a very muddy brook water containing much suspended matter, with

Calcium sulphate	8.1
Calcium carbonate	120.0
Magnesium carbonate	23.0

after standing forty-eight hours, the theoretical amount of aluminate removed ninety-six per cent. of lime and ninety-six per cent. of magnesia. One-half the theoretical amount removed 94.6 per cent. lime and 94.4 per cent. magnesia.

In treating the water from a well in Ashtabula, O., containing

Calcium sulphate	96
Magnesium sulphate	39

the theoretical amount of aluminate removed 98.3 per cent. of the lime and ninety-six per cent. of the magnesia.

A well in Glenville, O., containing

Calcium carbonate	99
Calcium sulphate	36
Magnesium carbonate	23

after treatment with theoretical aluminate showed that 98.1 per cent. of the lime had been removed and ninety-five per cent. of the magnesia.

To test still further the efficiency of the aluminate, experiments were made with sodium hydroxide alone, using various proportions, but the removal of lime was not much more than half the quantity taken out by aluminate, and the magnesia was not affected. An important effect of alumina is to remove suspended matter which it does rapidly and completely.

THE HEAT OF BROMINATION TEST FOR OILS.

By Augustus H. Gill and Israel Hatch, Jr.

Received October 5, 1898.

THIS test occupies a middle position between the Maumené and Hübl tests; it suffers from the disadvantages that the required apparatus is not always obtainable, and that the results obtained with different apparatus are not comparable. The object of the investigation was to simplify the apparatus and to ascertain if some substance could not be found with which the rise of temperature could be compared, and thus a "specific temperature reaction" obtained similar to the Maumené test.

Apparatus and reagents required; twenty-five cc. graduated flask; five cc. pipette; burette; thermometer divided into 0.2° calorimeter; measuring apparatus; bromine; carbon tetrachloride.

The calorimeter consists of a flat-bottomed glass tube about three quarters of an inch in internal diameter, and four inches long. This is held by a cork in a beaker two inches in diameter, thus making an air-jacket, and the beaker placed inside a four inch beaker, the space being filled with cotton waste; this cotton jacket guards against drafts.

The measuring apparatus is that devised by Wiley,[1] and consists of a filter bottle, through the neck of which passes the five cc. pipette carried by a rubber stopper. The side-neck is fitted with a blowing bulb; by pressing this bulb the liquid in the bottle is forced up into the pipette. One serves for the oil, and the other for the bromine solution.

The bromine solution is prepared by measuring from the burette one volume of bromine into four volumes of carbon tetrachloride, measured with the flask; it is kept in the filter bottle.

Five grams of the oil (ten grams of a tallow or neatsfoot oil and two and one half grams of a drying oil) are weighed out into the twenty-five cc. flask, and made up to the mark with carbon tetrachloride; it is then poured into the measuring apparatus. Five cc. of this solution are accurately withdrawn and run into the calorimeter, care being taken not to allow it to flow down the sides. The thermometer is inserted and, when the temperature has become constant, the reading is taken. Five cc. of the bromine solution measured out similarly to the oil, are allowed to flow down the sides of the calorimeter and mix with the oil; the reaction is instantaneous, and the highest temperature is noted. The mixture is poured out of the calorimeter, the latter wiped out, and allowed to cool before further use. At least three observations should be made, and the results should agree within 0.5°.

Notes: During the addition of the bromine solution to the oil the mixture should not be stirred, as the hot liquid will be cooled by contact with the sides of the calorimeter.

As in the Maumené test, the two solutions should be at the same temperature, which they will be if kept in the same room.

It was found that the bromine solution did not keep well longer than two days; hence a large quantity should not be prepared at one time.

Chloroform gives a slightly higher rise than over carbon tetrachloride, as would be expected; this was found to be 1.7° with the apparatus here described. Archbutt[2] and Jenkins[3] find

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[1] This Journal, 18, 378.

[2] *J. Soc. Chem. Ind.*, 16, 309.

[3] *Ibid.*, 193.

that the presence of water either in the bromine or the oil is apparently of no influence.

The results obtained vary with each calorimeter; hence to make them comparable they must, as in the Maumené test, be referred to some standard. Such a standard has been found in sublimed camphor, which can be prepared in sufficient purity; seven and five-tenths grams are dissolved in carbon tetrachloride and brominated, giving an average rise of 4.2°. The rises in temperature obtained with the various oils were divided by this number, giving a specific temperature reaction; if this be multiplied by a factor—found by dividing several of the iodine numbers by this specific temperature—the iodine value of any sample may be quite closely determined; this is shown in the following table, the factor being 17.18.

TABLE SHOWING THE RELATION OF THE BROMINATION AND IODINE VALUES.

		Iodine.	
Name of oil.	Spec. temp. Reaction.	Calculated.	Found.
Neats-foot	3.286	56.5	59.1
Tallow	3.348	57.4	57.2
Prime lard	3.715	63.8	63.8
Sperm	4.191	72.1	73.2
No. 1 lard	4.096	70.3	73.9
Olive	4.762	81.8	82.0
Cottonseed	5.667	97.3	103.0
Corn	6.381	109.5	107.8
Cod	8.002	137.4	135.0
Linseed	9.049	155.6	160.0
25° paraffin	1.643	28.2	10.1
300° lantern	1.190	20.5	0.0

In the case of the hydrocarbon oils the discrepancy may be due to the fact that there is substitution by the bromine and none with the iodine.

MASS. INSTITUTE OF TECHNOLOGY,
October, 1898.

THE ANALYTICAL CONSTANTS OF AMERICAN LINSEED OIL.

BY AUGUSTUS H. GILL AND AUGUSTUS C. LAMB.

Received October 5, 1898.

GENUINE samples of linseed oil having been found to yield lower iodine values than were usually accepted, it seemed desirable to determine the constants of some American oils of undoubted purity.

Nearly all the principal brands in the market were represented, being obtained from leading manufacturers in the east and west, whom we here wish to thank for their courtesy. The methods employed were those in common use, described at length in a little book by one of us[1]; it was found necessary in applying the Maumené test to mix the linseed oil thoroughly with a heavy petroleum and allow to stand an hour or two before the treatment with sulphuric acid, correcting for this in the rise obtained.

The results are given in the accompanying table and are the mean of two closely agreeing determinations.

CONSTANTS OF LINSEED OIL.

Brand.	Specific gravity at 15.5°C.	Valenta test °C.	Maumené test, °C.	Iodine absorption in per cent. in 4 hrs.	Iodine absorption in per cent. in 18 hrs.	Drying test, hours required.
1. Western raw	0.933	79	97	174.7	180	72
2. " "	0.932	70	90	169.7	180	72
3. " " special ...	0.934	73	105	178.0	178	72
4. Old Calcutta	0.931	71.5	106	167.5	178	72
5. Eastern oil	0.931	73	105	168.0	168	72
6. Western boiled	0.936	74	100	178.8	178.8	18
7. Eastern "	0.938	59.5	101	169.5	171	18
8. Acid bleached..........	0.934	52.5	103	160.0	160	84
9. Bleached without acid .	0.932	60	105	162.0	162	84
10. Menhaden oil..........	0.934	73.5	135	157.0	181	84
Usual constants.......	0.931–0.937	57–74	103–126		170–188	
Average.....	0.934		111		176	

Samples 1, 6, and 8 are from the same house, as also are 5 and 7; sample 10, menhaden oil, was examined because it is used as a substitute for, and an adulterant of, linseed oil. Its effect would be to raise the Maumené test, lower the iodine value, and retard the drying properties of the oil. It will be noticed that the constants here given differ from those usually accepted in that the Maumené and iodine tests are about ten and four per cent. lower, respectively.

It is to be noted further that, contrary to the experience of Dieterich[2], the iodine value is not, in the majority of cases, perceptibly increased by eighteen hours' standing.

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[1] Gill: A Short Handbook of Oil Analysis.

[2] *J. Soc. Chem. Ind.*, 12, 381.

ON A BALANCE FOR USE IN COURSES IN ELEMENTARY CHEMISTRY.

BY C. E. LINEBARGER.

Received June 16, 1898.

IT is now probably almost universally recognized that an elementary laboratory course in chemistry should include some experiments involving the use of the balance; that quantitative as well as qualitative work should be done by the student. Indeed, it seems that the fundamental laws of the science could not be really appreciated without some quantitative experiments being performed. Of course, such work cannot be done with expensive and delicate balances, as the beginning student has neither the time nor the requisite skill to handle them, not to speak of the cost. I think it will be admitted that a balance weighing to a centigram or so is all-sufficient. The balance should also weigh rapidly, and, as generally the weighing is done at the desk where the student does the rest of his work, the balance should take up a minimum amount of room, and should allow of frequent removal from desk to desk without getting out of adjustment.

One of the most vexatious things about the use of a balance in elementary classes is the loss and deterioration of the weights. No matter how careful instructors and students may be, weights will get lost or will have acid spilled upon them; and their replacement is, to say the least, bothersome. A balance that is not subject to this evil and is at the same time rapid, compact, and sufficiently accurate is shown in the accompanying cut.

As is seen, it has unequal arms, their ratio being as four is to one. The longer arm twenty cm. is divided into 100 equal parts, notches being made at the points of division. The weights consist of three riders weighing 25, 2.5, and 0.25 gram, respectively; in weighing, the positions they occupy when equilibrium is attained, show at a glance the desired weight. Thus, the reading in the cut is 7.42 grams. The riders are given a ring-shape so that they form an integral part of the balance; they are thus secured against loss. When any of them are not needed, they may be placed on a horizontal arm above the beam and are thus out of the way; their sizes are such that they slip easily through one another. The capacity of the balance is 111.0 grams; it is sensible to 0.005 gram with no load, and to about 0.01 gram with an average load. The up and down motion of the pan is so slight and the lateral motion of the beam so limited by stops that but little damage can be done to the steel knife edges, even though a careless student might perchance throw the object to be weighed upon the pan. Not only is the room taken by the balance itself small, but the room that would be occupied by weights is entirely spared. To prevent corrosion as much as possible, most of the parts are lacquered in black with white and gold lettering; not only is this finish durable, but it also prevents, in a measure, the balance appearing old from usage.

The balance is made by the Chicago Laboratory Supply and Scale Company, 31–45 West Randolph Street, and will be known as the "Chaslyn Balance."

THE DETERMINATION OF POTASH AS PERCHLORATE.

By F. S. Shiver.

Received July 14, 1898.

THE increasing use of potash salts for fertilizing purposes has made the determination of potash a question of prime importance to the agricultural chemist.

The desire to devise a method at the same time rapid and accurate has been manifested in many ways in the past few years, especially in Germany, the seat of the great potash deposits.

The German chemists believe they have solved the problem in the so-called Stassfurt method, which as all know permits of the separation of the potash by platinum chloride after previous precipitation of sulphuric acid by barium chloride in slight excess, and in a strongly acid solution. This method with practice is quite accurate and rapid, with a slight tendency, however, to high results in my hands. It possesses little advantage over the Lindo-Gladding method, in so far as rapidity and accuracy are concerned.

The following determinations were made by the Stassfurt method—potassium sulphate, C. P., and potassium chloride, C. P., were mixed with such impurities as to imitate the composition of commercial sulphate of potash, sulphate of potash and magnesia, kainit, and muriate.

TABLE I.

	K_2SO_4 used. Gram.	K_2SO_4 found. Gram.	Error on K_2SO_4. Gram.	Error on K_2O. Gram.
Sulphate of potash	0.3284	0.3291	+0.0007	+0.0004
		0.3289	+0.0005	+0.0003
Sulphate of potash and magnesia	0.1856	0.1863	+0.0007	+0.0004
		0.1870	+0.0014	+0.0008
Kainit	0.1000	0.1003	+0.0003	+0.0002
		0.1009	+0.0009	+0.0005
	KCl used. Gram.	KCl found. Gram.	Error on KCl. Gram.	Error on K_2O. Gram.
Muriate	0.2506	0.2498	—0.0008	—0.0005
	0.2522	0.2514	—0.0008	—0.0005

The factor used for converting potassium platinichloride into potassium sulphate was 0.35694 which is practically the same acid, the residue stirred with twenty cc. of hot water after which perchloric acid is added in quantity not less than one and a half times that necessary for the decomposition of all salts present.

The solution is now evaporated with frequent stirring to a sirupy consistency, some hot water is again added, and the solution evaporated still again with occasional stirring until the disappearance of all odor of hydrochloric acid, and till the appearance of white fumes of perchloric acid. An evaporation of large quantities of perchloric acid is to be avoided. If this takes place, more perchloric acid is to be added.

The cooled, more or less sirupy, contents of the dish are well stirred up with about twenty cc. of wash alcohol (ninety-six per cent. alcohol containing two-tenths per cent. perchloric acid), taking care however not to reduce the potassium perchlorate to a fine powder. After the alcoholic solution has become clear, it is decanted through the asbestos filters, the washing repeated with the same quantity of wash alcohol, allowed to settle and decanted again.

The residue remaining in the dish is freed of alcohol by gently warming, evaporating again with about three-tenths gram of perchloric acid and a little water, and washing the cooled mass with several cc. of alcohol, with which it is also brought into the filters and the perchlorate in the tubes finally covered with a little pure alcohol. The potassium perchlorate obtained in this way contains, according to Caspari, no phosphoric acid, or only slight quantities of the same ; on an average only 0.00057 gram phosphoric acid.

In the separation of sulphuric acid, Caspari seeks to avoid, as much as possible, a loss of potash, since he precipitates in a strong hydrochloric acid solution at the boiling temperature with a concentrated solution of barium chloride, made acid with hydrochloric acid. Experiments of the author prove also the applicability of the method in the presence of other acids not volatile on the water-bath, as chromic acid, and also boric, tartaric, and oxalic acids. If ammonium salts are present they are to be removed either with soda-lye or milk of lime, by gentle heating or through careful ignition.

A. Kreider[1] has followed the method as described by Caspari, and has obtained very satisfactory results. Kreider found the Gooch crucible preferable in the filtering of the perchlorate and recommends the same instead of the tubes proposed by Caspari. In the presence of phosphoric acid, the previous separation of which is not necessary, it appeared advisable according to Kreider's experiments to allow the perchlorate precipitate to stand with an excess of perchloric acid before treating with alcohol.

Six determinations made of potassium unmixed with other bases or non-volatile acids gave the following results:

In two cases the theoretical amount of potash (K_2O) was recovered as perchlorate; in three cases there was a loss of 0.0002 gram; and in one case a loss of 0.0003 gram; one-tenth gram of potassium chloride was operated on in all cases. In order to repeat Kreider's work, and to ascertain the accuracy of the process the following work was undertaken. A solution of chemically pure potassium chloride was prepared by dissolving 1.0005 grams in 200 cc. water. One cc. of the solution was found to contain 0.005 gram potassium chloride, aliquot portions being measured from a burette, evaporated, dried, and weighed.

In all the work here reported the method as proposed by Caspari with the use of the Gooch crucible as suggested by Kreider was employed.

However in the first three experiments reported the perchlorate was collected on paper filters as suggested by Wense, washed in the usual way, dried, and the perchlorate dissolved in hot water, and the solutions evaporated to dryness in platinum dishes and weighed.

In all cases the weighed perchlorate was a little discolored, due to the fact that the paper filters had been acted on to a slight extent by the perchloric acid, causing them to char a little around the edges during the process of drying. In the subsequent leaching with hot water, some of this carbonaceous material dissolved, and went in solution with the perchlorate.

The results obtained by weighing in dishes as above described were as follows:

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[1] *Am. J. Sci.*, 49, 443.

TABLE I.

	KCl solution used. cc.	Equivalent to KCl. Gram.	KCl found. Gram.	Error on KCl. Gram.	Error on K_2O. Gram.
I	6.2	0.0310	0.0310	+0.0000	+0.0000
II	8.1	0.0405	0.0411	+0.0006	+0.0004
III	5.0	0.0250	0.0253	+0.0003	+0.0002
Average		0.0322	0.0325	+0.0003	+0.0002

It will thus be seen that the average error in these determinations is 0.0003 gram KCl; it is possible that this slight plus error is due to the slight discoloration already noticed, and the weighing in dishes is not to be recommended though the results obtained are sufficiently accurate for all practical purposes. In the other experiments which follow the potassium chloride was weighed out directly for analysis, and the perchlorate was collected always in a Gooch crucible.

TABLE II.

	KCl used. Gram.	KCl found. Gram.	Error on KCl. Gram.	Error on K_2O. Gram.
I	0.0848	0.0859	0.0011	+0.0007
II	0.0217	0.0217	0.0000	0.0000
III	0.0419	0.0413	—0.0006	—0.0004
IV	0.1007	0.1009	+0.0002	+0.0001
V	0.1003	0.1015	+0.0012	+0.0008
VI	0.1016	0.1015	—0.0001	—0.0000
VII	0.0217	0.0210	—0.0007	—0.0004
Average	0.0675	0.0677	+0.0002	+0.0001

In the above determinations No. I was among the first made, and it is possible that the slightly high results obtained were due to lack of familiarity with the method. Excluding No. I, the average would be as follows:

KCl used. Gram.	KCl found. Gram.	Error on KCl. Gram.	Error on K_2O. Gram.
0.0647	0.0647	0.0000	0.0000

It would thus appear that the determination of potash as perchlorate in mixtures free from other bases and non-volatile acids, is quite accurate, equally as much as the determination by platinum salt.

After nitrogen and phosphoric acid, potash is the compound one has mostly to determine in fertilizers, plants, and soils. The potash is usually combined with sulphuric, nitric, or carbonic acid, and more rarely with phosphoric acid.

These salts are almost always associated with alkaline salts and the alkaline earths. It is now therefore a question of the applicability of the perchloric acid method to the determination of potash when associated with these other bases, and non-volatile acids, such as sulphuric and phosphoric acid. In regard to the bases it has been contended by some that magnesia is a disturbing element in the determination of potash by perchloric acid.

Schloesing has shown, however, that in the following mixture, after the removal of sulphuric acid by barium chloride and conversion of bases into perchlorates, the magnesia did not have any disturbing effect.

	Gram.
Potassium chloride	0.0835
Magnesium sulphate	0.5740
Sodium chloride	0.1298
Calcium chloride	0.2330

In this mixture, there was recovered, by proceeding as above stated, 0.0814 gram potassium chloride. Kreider has also shown that magnesia has no disturbing effect. He treated 0.1500 gram magnesium carbonate with perchloric acid, evaporated till fumes of perchloric acid appeared and cooled, when magnesium perchlorate crystallized; on treating this with alcohol a perfectly clear solution was obtained. It was also thought that it was necessary to remove all non-volatile acids, previous to the separation of the potash as perchlorate. Caspari and Kreider have, however, shown that it is only necessary to remove sulphuric acid. In order to secure a nearly complete separation of phosphoric acid from the potassium, Kreider has shown that a considerable excess of perchloric acid should be left upon the potassium perchlorate before it is treated with the alcohol.

Kreider's results on a mixture containing

	Gram.
Potassium chloride	0.1
Magnesium sulphate	0.13
Aluminum sulphate	0.05
Sodium phosphate	0.4
Calcium carbonate	0.13
Ferric chloride	0.05
Manganese dioxide	0.05

were quite promising as will be seen from the results reported in the *American Journal of Science*, **49**, 448.

The method as modified by Caspari and Kreider is quite promising, and I hope in the near future to do some further work on the determination of potassium associated with other bases and non-volatile acids.

Preparation of Perchloric Acid.

As perchloric acid is not a regular article of commerce it becomes necessary for each one desiring it to make his own supply. There may be mentioned briefly four methods for its preparation and the literature in which detailed directions may be found.

The Method as Proposed by Schloesing.—Prepare first potassium perchlorate from potassium chlorate by heating in the usual way. The mass after the decomposition of the chlorate is treated with boiling water, and then rapidly cooled; the crystals of potassium perchlorate separate; the potassium chloride remains in solution with some of the perchlorate also. The perchlorate is then dissolved and treated with sufficient quantity of hydrofluosilicic acid to obtain the potassium fluosilicate, the perchloric acid being liberated. After standing a while the precipitate is filtered off, and the filtered solution containing the perchloric acid is concentrated and treated with ammonia. The ammonia salt is next decomposed by hydrochloric and nitric acids, and the solution then evaporated on a water-bath to a sirupy consistency.

The solution is left in this condition for a day or two, to separate further any crystals of potassium perchlorate it may contain. The supernatant liquid is then ready for use after a blank experiment has been conducted with the same.

Process of Perrey.—Perrey has sought to avoid completely the presence of potash in the reagent. He makes use of the principle recognized first by Sérullas that chloric acid, distilled, furnishes a third of its weight of perchloric acid. Barium chlorate, a salt easily prepared, is dissolved in water, and the solution precipitated with sulphuric acid, leaving the chlorate, however, in slight excess. After filtration the solution is concentrated and distilled, the distillate being collected for use as soon as white vapors show themselves in the body of the retort.

The product which one receives is contaminated with a little chloric acid and chlorine which can be expelled on the water-bath. The yield of perchloric acid is about the same as in the

Schloesing process. For details of these two processes consult Grandeau: "Traité d'Analyse des Matières agricoles," 1, 88–91.

Caspari's Method.—This method is quite similar in principle to the method described by Schloesing. Potassium chlorate is used as a basis, potassium perchlorate being prepared from it in the usual way. The potassium perchlorate dissolved in water is then treated with hydrofluosilicic acid at the boiling temperature, the reaction being as follows:

$$2KClO_4 + H_2SiF_6 = K_2SiF_6 + 2HClO_4.$$

The solution is then filtered on an asbestos filter under pressure, the clear filtrate evaporated on a steam-bath to small bulk, and allowed to stand for twenty-four hours, whereby is effected the separation of any remaining potassium fluosilicate or perchlorate. It is again filtered and diluted with an equal quantity of water and barium chloride added in slight excess to remove last traces of sulphuric acid and hydrofluosilicic acid. The clear supernatant liquid is then poured off and evaporated on a water-bath till white fumes of perchloric acid appear.

The solution is then, after allowing any potassium perchlorate that may be present to separate again, diluted with water and the excess of barium salt most carefully removed with sulphuric acid. The solution is allowed to stand for several days, then filtered through paper, and is ready for use.

For details of the process consult Wiley's Agricultural Analysis, 2, 290, and *Ztschr. angew. Chem.*, *1898*, p. 68.

Kreider's Method.—By far the most simple and rapid of all the methods proposed for the preparation of perchloric acid is that worked out by Kreider. The method depends upon the production of sodium perchlorate from sodium chlorate by heating, in the usual way, the subsequent decomposition of the sodium perchlorate by hydrochloric acid with the liberation of perchloric acid and the precipitation of sodium chloride which is separated by decantation or filtration. The filtered solution is concentrated on a water-bath till white fumes of perchloric acid appear, then cooled and diluted with water when it is ready for use.

It is manifest that the acid thus prepared is not chemically pure, since sodium chloride is not absolutely insoluble in hydrochloric acid, but if a portion of the acid prepared as above be tested with silver nitrate it will be readily seen that any sodium chloride which may have remained in solution, has been converted into perchlorate. Furthermore, unless the sodium chlorate used contained some potassium or on evaporation the acid was exposed to fumes of ammonia, the residue from the evaporation of a portion of the acid prepared as above, will be entirely soluble in alcohol, and the presence of any sodium perchlorate is therefore entirely unobjectionable.

I have in the course of my work on this subject prepared the acid by this method several times, and have always found the process very satisfactory, requiring but little time and attention. In my work, however, I found, as the result of blank determination on the acid thus prepared, a very small residue insoluble in alcohol for which in all cases corrections were made. This correction was very slight, and in no way condemns the process, since it is a very simple matter to determine it once for all on any lot of acid, and make the proper use of the same in the actual determination.

For detail of the process consult Kreider's article in the *American Journal of Science*, **49**, 445-446.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

IMPROVED APPARATUS.

BY J. L. SAMMIS.

Received October 10, 1898.

BURETTE.

THE frequent use of Mohr's burette with Geissler's glass stop-cock during the past summer called the writer's attention to two points which, it was thought, might be improved.

The handle of the glass stop-cock, as usually made, is turned toward the right. Right-handed persons usually find it easier to operate the stop-cock with the left hand and stir or shake the titrated liquid with the right. In order to facilitate this, the stop-cock of a burette was cut off and sealed on again with its handle toward the left. See Fig. 1.

In titrating, much care has to be exercised lest the mark upon the float should sink below the graduations on the scale of the burette. To render this impossible and to enable one to see more easily the scale and the titrated liquid at the same time, the tip of the burette was elongated to about fourteen inches by sealing in a piece of glass tubing between the stop-cock and the constricted extremity. This elongated tip was bent to the front and a little to the right just below the stop-cock, and then upwards. Two more bends were so placed that the end of the tip was about three inches in front and one inch to the right of the lowest mark upon the fifty cc. burette. By this arrangement, with the stop-cock wide open, not a drop of liquid will flow out after the liquid meniscus in the burette has reached the level of the end of the tip, which, as described, is just opposite the fifty cc. mark of the scale. If the tip be placed a little higher up, say opposite the forty-nine cc. mark, the instrument may be used with a float or without. The long narrow burette with the new tip can be held much closer to the table by the burette clamp, and the easy reading of the upper end of the scale is thereby facilitated.

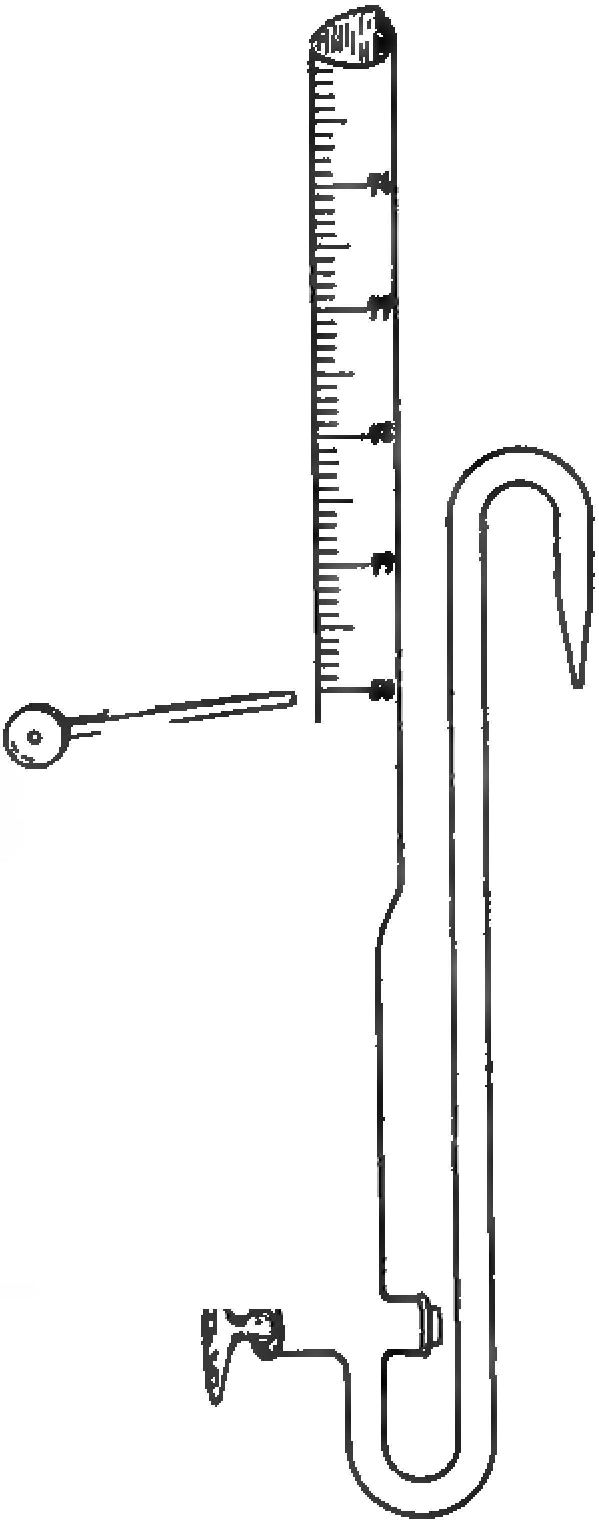

FIG. 1.

ELECTRIC HEATER ADAPTED FOR USE IN ETHER EXTRACTION.

During the past year, a large number of extractions with Sohxlet's apparatus have been performed in this laboratory. In order to continue this operation during the night time without the danger of fire, an electric heater was devised which could be put in operation by closing a switch and which kept the water at the proper temperature as long as desired. The heater (Fig. 2) is made of coils of No. 24, soft iron wire, wrapped upon a brass rod, and insulated from the rod and from each other by thin sheet asbestos. The winding was done rapidly by placing in the lathe chuck a brass rod six inches long and three-eighths of an inch in diameter, laying a sheet of asbestos paper over it, and winding on the wire, keeping the turns about one-thirty-second of an inch apart to prevent short circuiting. Having wound one coil, a second sheet of asbestos is put on, and a second coil wound on it, and so on until the desired resistance is obtained. The ends of the iron wire are soldered to short pieces of No. 12 insulated copper wire which serve to bring in the electric current. The cylinder thus made is slipped into a closely fitting tube of sheet copper and the ends of the latter are soldered on. A small hole or notch is left at one end of the copper tube through which the insulated wires pass. These copper wires are pushed through a narrow piece of brass tubing about four inches long, and the tubing is soldered to the copper cylinder in a position perpendicular to the axis of the latter. The heater is placed in a four-holed water-bath and the brass tube with the copper wires is pushed up through a small hole made in one corner of the top of the bath. The tube may be soldered to the

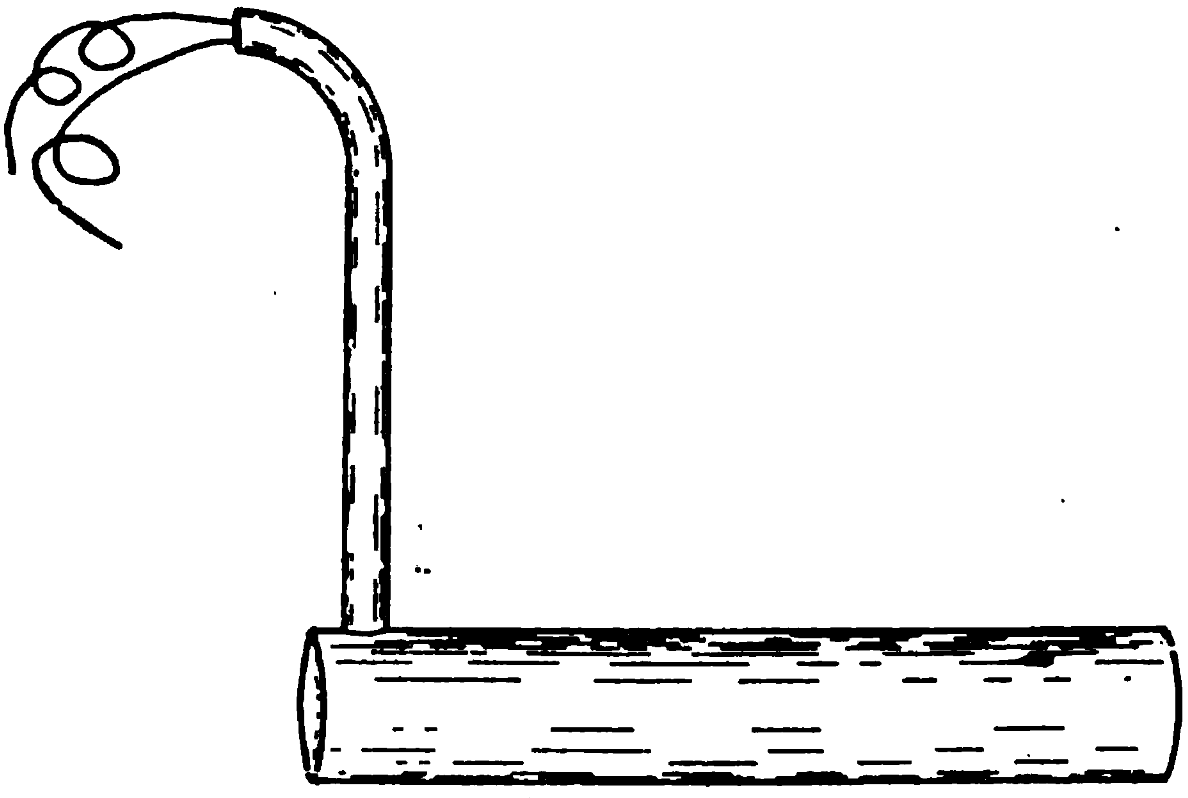

FIG. 2.

edges of the hole. The ends of the copper wires are made fast to binding posts, screwed into a narrow strip of wood upon the front of the battery of water-baths.

One heater is required for each four-holed water-bath, and the heaters are connected in parallel. The length of the iron wire in one heater is seventy feet, and its resistance when hot is twenty-six ohms. The potential difference across the ends of the heating coils is fifty-two volts, thus using two amperes of current and 104 watts per heater. The heat generated is sufficient to keep the water in the bath at 65° C., and the ether in the extraction apparatus falls from the condenser at the rate of twenty or twenty-five drops per minute. The currents from a storage battery and from a 125-volt dynamo have been used to run this apparatus with perfect success, and with little attention and no risk of fire.

September 25, 1898.

GLYCOLLIC ACID: ONE OF THE ACIDS OF SUGAR-CANE.

By Edmund C. Shorey.

Received September 26, 1898.

IN continuing work on organic non-sugar in sugar-cane, indicated in a paper[1] "On the Principal Amid of Sugar-Cane," glycollic acid was prepared from the sugar-cane amid by the action of nitrous acid,

$$CH_2NH_2COOH + HNO_2 = CH_2OHCOOH + N_2 + H_2O$$

and the acid so obtained compared in chemical and physical properties with glycollic acid obtained from other sources, monochloracetic acid, hippuric acid, etc. The samples of glycollic acid obtained in various ways were found to be identical in every respect with that obtained from the sugar-cane amid.

The presence of glycollic acid as such in sugar-cane was, in a sense, discovered by accident, and its isolation and identification is of considerable interest to the sugar manufacturer, the analyst, and the student of plant physiology. It was noted that on adding a few drops of strong nitric acid to a sample of cane juice, clarified for the polariscope in the usual way, with a slight excess of lead subacetate, a white crystalline precipitate was thrown down. This, on examination, was found to contain

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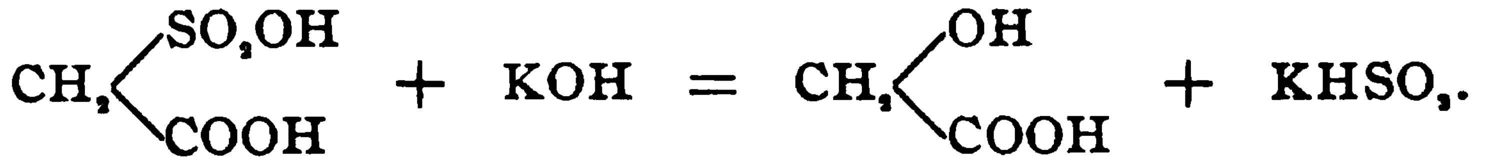
[1] This Journal, 19, 11.

lead, and on decomposing with hydrogen sulphide gave an acid solution, which, on evaporation to a sirup, deposited needle-shaped crystals, generally grouped in radiating clusters. These crystals were exactly the same in appearance as those of glycollic acid, which had been prepared from various sources, and were found to possess the same chemical and physical properties. To further verify the identity of the various preparations with glycollic acid, this acid was prepared by still another method; *viz.*, by the action of caustic potash on sulphonic acetic acid,



$$CH_2\left\langle\begin{array}{l}SO_2OH\\COOH\end{array}\right. + KOH = CH_2\left\langle\begin{array}{l}OH\\COOH\end{array}\right. + KHSO_3.$$

The glycollic acid formed in this case was the same in every respect as that which had already been prepared by other methods.

The crystalline precipitate thrown down by nitric acid appears to be a mixture of normal and basic lead glycollates, containing from sixty to seventy per cent. of lead. The isolation of glycollic acid from cane juice in this way is open to the objection that it may have been formed from glycocoll by the action of some nitrous acid in the nitric acid, and may not occur as such in the cane. To remove this objection, advantage was taken of the sparing solubility of the copper salt, and the acid has been isolated from cane juice in quite large quantities by the following method:

The fresh cane juice was treated with an excess of freshly precipitated cupric hydroxide, washed thoroughly with cold water by decantation, and the precipitate treated with hydrogen sulphide, filtered from cupric sulphide, and the resulting acid solution evaporated until crystals began to form, when, on cooling, a solid mass of crystals was obtained. By this method glycollic acid equivalent to from seventy-five to eighty per cent. of the total acidity of the juice has been obtained; but its value as a quantitative method has not been established. Glycollic acid prepared in the various ways mentioned has been obtained in four-sided needle-shaped crystals generally arranged in tufts, soluble in water, alcohol, and ether, with a purely sour taste not unlike that of tartaric acid. If great care be taken not to carry the evaporation of the solution too far, the crystals are quickly formed, are completely soluble in water again, are unchanged in the air, melt, turn brown, and decompose below 100° C., and give precipitates in neutral solution with lead acetate, mercuric nitrate, and cupric sulphate.

The most notable characteristic of glycollic acid is the ready formation of the anhydride. If the water solution be evaporated to dryness stopping short of the formation of brown color, the mass of crystals presents the same appearance as that obtained by careful evaporation noted above; but it rapidly deliquesces in the air, and on treating with water a portion is found to be insoluble as white flocks or as a white powder. This insoluble portion is the anhydride, part of which is dissolved by the acid remaining, resulting, if not too dilute, in a thick solution not unlike vaseline, from which needles of glycollic acid are slowly deposited. If the free acid be neutralized with caustic soda the whole of the anhydride is precipitated.

In some respects glycollic acid resembles malic acid, and might, in some cases, be confounded with it, but it differs at the following points:

1. Glycollic acid is more readily obtained in crystalline form.

2. It is optically inactive: natural malic acid appears to be always optically active, being right- or left-handed as it is more or less concentrated.

3. The lead precipitate obtained from neutral solution of glycollic acid is soluble in acetic acid and insoluble in strong ammonia.

4. On heating, glycollic acid chars and suffers decomposition, the chief product of which is formic acid. Malic acid decomposes into maleic and fumaric acids, which can readily be identified.

Aconitic acid has often been stated to be present in sugarcane, and for this reason the glycollic acid in cane juice might be mistaken for it, but they can readily be distinguished by the fact that aconitic acid melts at 140° C., boils at 160° C., decomposing into itaconic acid and carbon dioxide. I have before me, at the present writing, preparations of glycollic acid made in the following ways:

1. By the action of nitrous acid on glycocoll, obtained from hippuric acid.

2. By the action of nitrous acid on glycocoll obtained from sugar-cane.

3. Obtained directly from cane juice by treatment with cupric hydroxide and subsequent decomposition with hydrogen sulphide.

4. By the action of caustic potash on sulphonic acetic acid and isolation as the copper salt, as above.

These four preparations are exactly the same in appearance, and I have not been able to find any physical or chemical test, by which one can be distinguished from another.

To the sugar manufacturer the presence of glycollic acid presents the following points of interest: In evaporating cane juice in multiple-effect evaporators, acid vapors are sometimes given off and the free acid can be found in the condensed vapor from the following drum, or under other conditions the acid is found in this water in combination. In the *Planters' Monthly* (Honolulu), 15, 8, E. Hartmann has shown that these condensed vapors contain organic acids, chiefly formic, in combination with iron. Hartmann assumes that the formic acid results from the oxidation of sugar in the process of evaporation; but, as I have already noted, glycollic acid is decomposed below 100° C., giving formic acid as one product of decomposition, and it is quite possible for this decomposition to take place in cane juice under certain conditions.

The formic acid, given off on heating glycollic acid, I have identified by its general physical properties, its action on silver nitrate, and by its conversion into the copper salt, the anhydrous salt containing 41.1 per cent. copper. The exact behavior and conditions under which free glycollic acid and the calcium salt decompose, or undergo change, when heated in sugar solutions, are not yet determined, and, as subjects of future study, present possible explanation of several hitherto unexplained facts in sugar-house work. Three of these may be briefly noted:

1. It is known that if raw acid cane juice be boiled or evaporated, it becomes less acid, and it is also well known that starting with cane juice exactly neutral, the molasses from the second or third sugar may be quite acid, without any fermentation hav-

ing taken place. The ease with which glycollic acid is converted into the anhydride, which is a neutral body, and the fact that the anhydride, on long boiling with water, is converted into the acid again, have a very probable connection with these facts.

2. The natural coloring-matter of cane juice is quite different from that which results from the processes of sugar manufacture, and which causes largely the dark color of low-grade sugars and molasses. The former can be completely removed by lead subacetate, while the latter, which seems to partake of the nature of caramel, cannot, in many cases, be removed by any reagent. The ease with which glycollic acid chars or becomes brown when heated, explains probably the presence of a portion of this coloring-matter in low-grade products of the sugar house.

3. It is customary to boil low-grade molasses to a certain consistency known as " string proof," and molasses thus boiled is placed in coolers or wagons and allowed to remain until granulation has reached the point when the massecuite can be conveniently and profitably dried in centrifugal machines. It sometimes happens that in a short time, twenty-four to thirty-six hours after this massecuite has been placed in coolers or wagons, considerable frothing or foaming takes place, and a considerable portion of the massecuite runs over on the floor. In Louisiana, where it happens much more commonly than in Hawaii, this foaming is attributed to boiling at too high a temperature, 165° F. being considered the point beyond which it is not safe to go. In Hawaii this rule does not always apply, but when foaming takes place it undoubtedly is due to the decomposition of some body in the slowly cooling mass, and the gas resulting from this decomposition entangled in the viscous mass necessarily causes foaming. The presence of glycollic acid, a body easily decomposed at a comparatively low temperature, is not unlikely to be connected with this phenomenon.

To the sugar chemists the presence of glycollic acid in sugarcane presents at least two points of interest : First as a possible explanation of the formation of the color of low-grade sugars and molasses which every worker with the polariscope finds so troublesome to remove ; and second, as a probable explanation of the impossibility of accurately estimating the total solids in cane juice by evaporating to dryness. When cane juice is evaporated to dryness, even in a vacuum, some of the bodies contained suffer decomposition into gaseous products, giving a residue less than the actual weight of solids originally held in solution; the decomposition of glycollic acid is no doubt responsible for a portion of this loss.

The presence of glycollic or hydroxyacetic acid, $CH_2OHCOOH$, in sugar-cane is full of suggestions to the physiologist. The principal amid of sugar-cane, glycocoll, CH_2NH_2COOH, is very closely related to this acid; in what relation do they stand in the plant? Is one formed from the other or have they each their separate rôle in the plant economy? Glycollic acid is readily obtained by oxidation of dextrose or levulose and so from cane-sugar; does it stand in any relation to the building-up of the cane-sugar in the plant? Glycocoll and glycollic acid are comparatively simple methyl compounds; how close do they stand to the supposedly simple first product of carbon assimilation? These and numerous other questions present themselves, —questions, the answers to which extend over the whole realm of plant physiology.

LABORATORY OF KOHALA SUGAR CO.,
KOHALA, HAWAII, Sept. 8, 1898.

A NEW APPARATUS FOR THE DETERMINATION OF VOLUME.[1]

BY CHAS. F. MCKENNA.

Received November 15, 1898.

THIS instrument has been devised in order to obviate certain objectionable features of those others, whose type is the Schumann or Candlot Volumenometer. Such objections are:

a. The reading is not delicate, since the caliber of the tube is large. Such instruments are limited in accuracy by our ability to read to 0.01 cc. This is obviously impossible in such tubes.

b. The solid must be introduced through the liquid on the lines where the reading is subsequently made. The slight coating here formed on the walls of the tube tends to increase the difficulty of making this observation correctly.

c. The ground joint by which the tube fits into the flask

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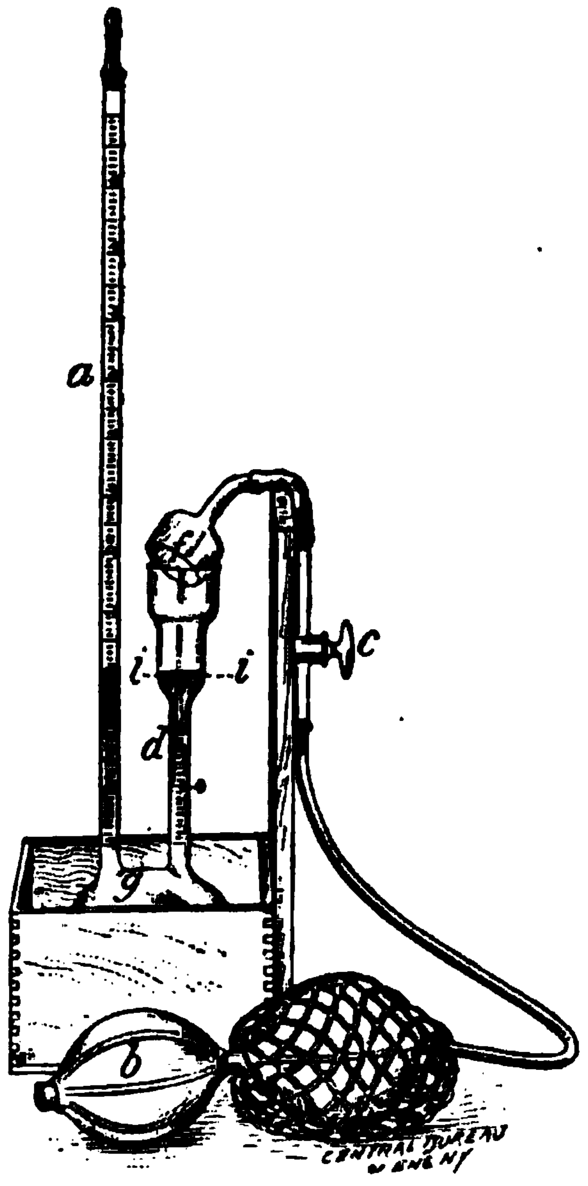
[1] Read at the meeting of the New York Section, November 11, 1898.

usually leaks when a liquid like benzine is used. Any apparatus with a stop-cock in contact with the liquid is open to the same objection. An English form, recommended by Stanger and Blount, in which the tube is blown with the flask, is a good one.

In the apparatus I propose, the solid is introduced by one tube and the change of volume is measured on another one so slender that tenths of a cubic centimeter can be easily read and the hundredths quite accurately estimated.

The flask *g*, of about 175 cc. capacity, has two vertical tubulures blown into it; one, *a*, of the inner diameter of a pipette stem (five mm.) graduated in cubic centimeters and tenths, topped by a perforated glass stopper, and the other, *d*, with its middle portion similarly graduated for one or two cc. above and below a 0 mark, and this expanding into a receiving-tube about twenty-five mm. in diameter, closed by a ground-glass stopper *f*, with a glass tube prolong. This prolong is connected to a glass stop-cock and further on to a rubber bulb. The stop-cock, it will be noticed, is quite outside of the liquid-holding part of the apparatus.



In making a specific gravity determination of a mineral or other material in powder, begin by filling the flask through the receiving-tube with liquid up to a line about *ii*. Then place the stopper in above this, blow gently with the bulb and close the stop-cock *c* when the liquid stands in the tube *d* at the 0 mark. From this to the top of the column in *a* is the initial volume and the reading on *a* is to be noted.

Then remove *f*; the liquid flows back to *ii*, and presents a wide surface down through which a definite weight of the finely divided and dried powder can be sifted by using such an article as a porcelain Gooch crucible or a similar object spun from brass and fitting into the opening. Now replace *f* and blow the liquid back. If any powder remains, the columns can be made to surge back and forth and carry every particle down. The column *d* is then forced down to 0, the stop-cock *c* turned to hold it there, and the reading taken at the top of the column in *a*.

To insulate the flask it is well to enclose it in a box and surround it with asbestos, sawdust, sand, or some such material that will guard against expansion or contraction of the volume of the liquid by the influence of surrounding things. Should the air or vapor in the space from the 0 mark to the stop-cock be subject to such influences any error from it is nullified by making a differential reading on the two columns. Thus, if the column is blown down to 0 and the reading in *a* is taken to be say 5.42, and a half minute afterwards it is noticed on stem *d* to be at —0.07, let *a* be immediately read again and it will be found to be

5.49
0.07
True volume as before, 5.42

Taking three sets of such readings on the initial volume and three on the final volume after the addition of the solid, conduces very much to accuracy and to a check upon one's estimations of the hundredths. Thus an actual case was:

Initial volume.	Final volume.
6.38—0.02 = 6.36	9.57—0.00 = 9.57
6.38—0.01 = 6.37	9.67—0.10 = 9.57
6.37—0.00 = 6.37	9.59—0.03 = 9.56
6.38—0.01 = 6.37	9.62—0.06 = 9.56
	9.67—0.10 = 9.57

An instrument, designed thus with longer stem to hold the increase of volume caused by fifty grams of material, would be more accurate than one designed for ten grams; but ten grams is a convenient weight, and when it is used a table of reciprocals hanging in front of the apparatus would enable one to read off the specific gravity at once upon noting the difference of volume, multiplying the reciprocal by ten.

In this way many delicate determinations of specific gravity can be made in immediate succession with considerable economy of time and labor.

NEW YORK, November 1, 1898.

[CONTRIBUTION FROM THE LABORATORY OF AGRICULTURAL CHEMISTRY, OHIO STATE UNIVERSITY.]

LIGHT A FACTOR IN SUGAR PRODUCTION.[1]

BY H. A. WEBER.

Received September 10, 1898.

THE fact that the United States is one of the greatest sugar-consuming nations of the world, and that about nine-tenths of the sugar consumed is imported at an annual cost of about $100,000,000, have given rise, from time to time, to attempts in the direction of a greater home production of sugar than is possible from the long-established sugar-cane industry of the Gulf States.

Owing to the geographical location of this country, only such sugar-producing plants could form the basis of these attempts, as were adapted to cultivation in the temperate zone. Of these plants only two need be mentioned here ; namely, sorghum and the sugar-beet.

As is well known the early efforts at sugar production from beets in this country were absolute failures. Various causes contributed to this result, prominent among which was the antipathy of the American farmer to accomodate himself to the cultivation of beets, which is much more irksome than the cultivation of ordinary agricultural crops, to which he had been accustomed, and which at that time brought him satisfactory returns for his labor. The country was not ripe for the establishment of the new industry.

In the late seventies and early eighties the experiments in making sugar from sorghum were at their height. This crop can be grown like corn, and its cultivation is much more in keeping with the tastes and practices of the American farmer, than that of the sugar-beet. Wherever sorghum sugar factories were established there was no difficulty whatever in securing an abundant supply of the cane delivered in proper shape at the mills. For a time the prospects of the sorghum sugar industry were bright. The sugar produced found a ready sale at remunerative prices, but, unfortunately for those who had embarked in the new enterprise, and fortunately for those who

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[1] Read at the Boston Meeting of the American Association for the Advancement of Science.

were about to invest on a larger scale, the sorghum sugar industry, before it was fairly upon its feet, was confronted by a falling market, due to the overproduction of sugar in Europe and especially in Germany. This unexpected interference with the sugar market of the world, gradually brought the price of sugar and molasses down to a point where the manufacture of sugar from sorghum was no longer profitable, and the new industry which had excited general attention for three or four years had to succumb with all its investments, a total loss. It may be said in passing, that the sorghum sugar industry is dead for all time to come. The good old times for the manufacture of sugar, when yellow C sugar sold for eight cents per pound cash in car-load lots, are gone nevermore to return.

These fruitless attempts at the establishment of a sugar industry in this country have been thus briefly referred to, for the reason that they are still of importance to us for the lessons which they have taught.

The Department of Agriculture at Washington, under the able direction of Dr. Wiley, has for many years made valuable investigations in connection with the sugar industry; but with the advent of the present Secretary of Agriculture, a general interest in the subject of a home production of sugar has been renewed. The efforts of Secretary Wilson found the farmers throughout our country in a responsive mood, owing to the universal depression in agriculture for a number of years preceding his administration, and consequently during the past year in almost every county of many of the states, experimental plots of sugar-beets were grown.

Whether the establishment of this new agricultural industry in our country is advisable from an economic point of view or not, is a question foreign to this paper. This phase of the subject was ably discussed by Mr. Edward Atkinson in the *Forum* of November, *1897*, in an article which deserves the earnest consideration of all who are interested in the public welfare.

If, however, the efforts put forward should result in the establishment of a beet-sugar industry in this country capable of producing our home demand for sugar, it should be borne in mind that this object must be accomplished in the face of an overproduction of sugar in the world, a condition which twenty years ago would not have been considered possible. This overproduction of sugar has come to stay. The margin of profit will necessarily be low. Of our vast domain the insignificant area of 2,000,000 acres of land subjected to beet culture will suffice for the production of our home demand for sugar. Taking all these facts into consideration it is evident that the successful sugar factories will necessarily exist only in the most favorable localities, and in the course of a very short time factories blindly started in unfavorable localities will be crushed.

There are various conditions, which must be supplied for the production of a sugar-producing plant rich enough in sugar to meet the competition at present existing in the manufacture of this article of food, as well as certain facilities for operating a factory after the plants are grown. Prominent among the former conditions is the matter of light. The leaves are the laboratory in which the sugar is directly or indirectly synthesized and light is the agent.

All sugar-producing plants are equipped by nature with an abundant leaf surface, and when these plants are rescued from their unfavorable surroundings in wild vegetation and subjected to cultivation, their leafy organs are capable of elaborating and storing much more sugar than is necessary for the perpetuation of the species. This excess of production is utilized by man for the manufacture of sugar.

It would seem evident therefore that, other things being equal, the more light one of these plants could get during its period of vegetation, the higher its content of sugar would be. The truth of this proposition has been confirmed by numerous observations made upon sugar-producing plants.

Sugar-producing plants may be divided into two categories: (1) Those having a long period of vegetation, as the different varieties of southern cane, and (2) those having a short period of vegetation as sorghum and the sugar-beet. The former group of plants when cultivated in tropical regions grow luxuriantly for a period of eighteen months and at the end of this time the content of sugar in the juice reaches eighteen to twenty per cent. The crop of sugar-cane is, however, usually taken off after a period of twelve months, when the content of sugar in the juice is only fourteen to fifteen per cent.

The increase in amount of sugar in the longer period of vegetation is due to the greater amount of sunlight, to which the growing plants have been exposed. Owing to this long period of vegetation, southern cane is not so much affected by climatic conditions and suitable locations as is the case with plants of a short period of vegetation.

The latter group of sugar-producing plants, in which the present territory of this country is directly interested, are affected in many ways by the amount of light available during the period of vegetation, which on account of the present competition in the manufacture of sugar may mark prospective enterprises with success or failure as the case may be.

1. Climatic conditions must be taken into consideration in the location of sugar factories. Localities in which the seasons vary greatly in the amount of clear weather are not so well adapted to the growing of rich sugar plants as those in which clear weather during the growing season predominates every year. As an example illustrating this fact may be mentioned the experience of the writer in the investigation of sorghum as a sugar-producing plant.

The years 1880, 1881, and 1882 in the locality of Champaign, Illinois, were typical sugar seasons. During the summer months clear weather prevailed. The cane-sugar in the juice of the best varieties of sorghum reached thirteen to fourteen per cent. The coefficient of purity of the juice was high, and with proper precautions in treating the juice, sugar could readily be made even with crude apparatus. The years following were less favorable in this respect. In 1883, for example, cloudy weather with rain prevailed almost daily during the summer months. As a consequence the content of cane-sugar in the juice of the better varieties of sorghum only reached eight to ten per cent. The purity of the juice was correspondingly low, and the manufacture of sugar extremely difficult.

Four sorghum sugar factories were erected in consequence of the favorable results obtained in the preliminary experiments of 1880 and 1881 at Champaign, Illinois, conducted by Professor M. A. Scovell and the writer. It is safe to say, that if the weather of these two seasons had been similar to that of 1883, the factories would not have been started and the capital and labor invested in them lost.

The ideal localities in this respect are the arid plains of the western states, where the necessary soil moisture can be supplied by irrigation. Here, for a given degree of latitude, the maximum amount of light is available for the growing crop, and poor sugar seasons cannot occur.

2. The higher latitudes are more favorable, other things being equal, than the lower ones, owing to the greater length of the days and the longer duration of twilight.

The sorghum sugar industry again can furnish data illustrating this point. Among the numerous visitors from all parts of this country and from many foreign countries to the factory at Champaign, Illinois, was a party from Tennessee, who claimed that the "Sunny South" was the place for raising sorghum. Capital was raised, a factory erected at Franklin, Tennessee, and about 700 acres of sorghum were grown. The yield of the crop was heavy; but the sugar content of the juice was very disappointing, it being about four per cent. lower than that of sorghum grown in central Illinois, although the season was an ordinary one for that section of the country.

The plant from which the sugar-beet has been derived is indigenous along the shores of the Mediterranean Sea, but it has been developed into one of the most important sugar-producing plants in the latitudes of northern Germany and France.

The writer does not wish to be understood as claiming that a higher latitude is under all circumstances better than a lower latitude. The climatic conditions already mentioned, and other conditions to be considered further on, may more than compensate for the increase of light obtainable through a more northerly location.

3. Proximity to large bodies of water is favorable to sugar production. This is due to the fact that near the shore of such bodies of water and extending for a considerable distance inland, the location has the advantage of a more intense light, caused by the direct rays of the sun in addition to the light reflected from the surface of the water. The writer had an opportunity of investigating this point during the past season.

Sugar-beet seed of the Klein-Wanzleben variety was universally distributed over the state of Ohio by the Department of Agriculture at Washington, and also very generally planted for experimental purposes. Samples of beets were obtained representing a section of the state from Lake Erie to the Ohio River. A sample consisted of four average beets of each field or plot from the largest size down to about one-half pound in weight. Each beet was wrapped in paper and the sample sent by express to our laboratory, to insure as slight a change as possible, and immediately analyzed. In addition, and in order that the results obtained might be strictly comparable, the percentage of juice was determined in each case.

Without going into details, the results of the investigation clearly indicate that the region of the state of Ohio bordering upon the lake has advantages in the raising of sugar-beets of high grade, which are not possessed by other portions of the state. The best samples of beets in the whole list were grown at Oak Harbor near Lake Erie. The smallest beet weighed twenty ounces and the largest twenty-nine ounces. The percentage of sugar in the juice was 16.3 and in the beets 15.68. The coefficient of purity was 81.71.

A sample grown at Locust Point on the lake exemplifies, in a high degree, the possibilities of the lake region in producing beets with a high content of sugar. The smallest beet of the sample weighed twenty-eight ounces and the largest 71.25 ounces or nearly four and five-tenths pounds. The percentage of sugar in the juice was 14.2 and in the beets 13.8 with a coefficient of purity of 81.42.

The same may be said of another sample grown at Locust Point. The smallest beet of this sample weighed 60.25 ounces and the largest 70.25 ounces. Even these enormous beets with an average weight of four pounds were found to be above the standard for content of sugar and purity of the juice, as generally accepted for the manufacture of sugar.

The remarkable richness of these overgrown beets becomes more apparent, when contrasted with a sample grown in Licking County in the central portion of the state. This beet weighed 40.75 ounces; the content of sugar was 8.47 per cent., and the purity 64.68 per cent.

Although some samples were obtained from other sections of the state, which were of good quality for the manufacture of sugar, yet other samples of the same sections fell below the standard. The lake region alone produced beets, which were uniformly of a high grade, when all the requirements of a good beet were taken into account.

4. Topographical features of land are of importance in determining a suitable location for a sugar factory. It is well known that beets grown in the shade are worthless for the manufacture of sugar. In view of this fact it would seem almost superfluous to say that a partial obstruction of the direct rays of the sun daily would cause the production of a crop of beets of lower sugar content than would be the case if such obstruction did not occur. Consequently level tracts of land, where on clear days the plants are exposed to the direct rays of the sun from morning to night, must be better adapted to beet culture than deep valleys, especially if they are narrow and skirted by hills or mountains, and if in addition their general course is from north to south.

The writer is convinced that the variation in the composition of beets grown in the same sections of the country, having a diversified topography, is due in a great measure to the injudicious selection of the fields in this respect.

There are other factors which enter into the successful inauguration of the proposed new beet-sugar industry in this country, but, as a guide to the selection of the most favorable localities for its permanent establishment, the matter of light should receive due consideration.

COMMERCIAL IRON SILICIDES WITH A HIGH PERCENTAGE OF SILICON: THEIR PROPERTIES, MANUFACTURE, AND USES.

BY G. DE CHALMOT.

Received August 26, 1898.

IRON silicides containing about eleven to thirteen per cent. silicon have, for some years, been made in blast-furnaces, and have been successfully introduced in the manufacture of iron and steel. It has been found impracticable to much increase the amount of silicon by the blast-furnace process. This can, however, be successfully done by changing the process and making use of the great heat of the electric furnace. I have made, in the electric furnace, silicon-iron alloys containing from twelve to forty-six per cent. silicon. In alloys up to 46.5 per cent. silicon, and most probably in those up to fifty per cent. silicon, the iron and the silicon are chemically combined; *i. e.*, there is no free silicon and no free iron present. If more than fifty per cent. silicon is forced into the iron, the excess crystallizes out in small black crystals. This article deals only with silicides containing twenty-five to fifty per cent. of silicon.

COMPOSITION.

Silicides of from twenty-five to fifty per cent. silicon seem to consist of a mixture of two distinct compounds between iron and silicon; compound *a*, which contains twenty-five per cent., and compound *b*, which contains fifty per cent. silicon. These compounds are represented by the chemical formulas Fe_3Si_2 and $FeSi_2$. Both these compounds were obtained pure enough for analysis. When iron silicides with about twenty-five to twenty-eight per cent. of silicon are allowed to cool slowly from the liquid condition, compound *a* will crystallize out in very well-developed crystals, some of which will be as large as one-half inch to the side. These crystals have never been determined crystallographically. They have, among others, well-developed tetrahedral faces. These crystals are best obtained from an alloy containing from one to two per cent. silicon above twenty-five per cent. It is probable that some iron-silicon compound containing less than twenty-five per cent. silicon hinders the crystallization of the compound Fe_3Si_2.[1] Crystals obtained at various times and in different furnaces contained:

	1. Per cent.	2. Per cent.	3. Per cent.	Composition of Fe_3Si_2. Per cent.
Iron	74.75	....	75.89	75.00
Silicon	25.17	25.30	24.48	25.00

To isolate the compound *b*, I make use of the fact that acids attack the silicide faster the lower the content of silicon. I used a silicide containing about thirty-nine per cent. silicon, and which, according to my views, contains fifty-six per cent. of compound *b*, and forty-four per cent. of the compound *a*.

The acid used was hydrofluoric acid. This acid attacks both

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[1] A most beautiful specimen of these crystals can be seen at the New York office of the Willson Aluminum Co. It is a piece of silicide of fifteen inches in diameter, on one side entirely composed of these crystals, some being among the best developed that were ever produced.

compounds rather easily, and in order to obtain any residue I had to work carefully and with moderation. The finely pulverized silicide was suspended in water and the acid added in successive small amounts. By thorough cooling, a too violent reaction was prevented. The acid added was not sufficient to dissolve the whole of the silicide. The residues, which were thus obtained, contain :

	1. Per cent.	2. Per cent.	3. Per cent.	Composition of $FeSi_2$. Per cent.
Iron	50.56	52.24	....	50.00
Silicon	49.71	48.26	49.35	50.00

The yield of residue was about twenty per cent. of the amount taken. Compound *b*, thus obtained, forms a gray crystalline powder quite unmagnetic.

I have obtained in the furnace an alloy containing : Iron 53.76 per cent., and silicon 46.22 per cent., which corresponds to a content of 84.88 per cent. of the compound *b*. This alloy was gray and crystalline, and could be easily pulverized.

Hahn has described an iron silicide of fifty per cent. silicon, which he produced in minute quantities by treating a twenty per cent. silicon alloy with hydrofluoric acid. He describes this compound as insoluble in hydrofluoric acid; hence it is different from that which is found in my silicides. It was produced in an entirely different manner.

Among the combinations more likely to be present in my silicides, might be the compound FeSi with 33.3 per cent. silicon. Such a compound has been described by Hahn and by Fremy. It is not easy to show with certainty that such a compound is not present in these silicides, where we have to deal with a mixture of compounds having similar properties. It seems probable that this compound does not exist in my silicides. An alloy containing 31.4 per cent. silicon was taken. If the compound of 33.3 per cent. silicon existed, it would be present especially in this alloy in large quantities. We might expect this compound to contain 22.9 per cent. of compound *a*, of twenty-five per cent. silicon, and 77.1 per cent. of the compound with 33.3 per cent. silicon. On the other hand, if the compound of 33.3 per cent. silicon is not present the alloy would contain 74.4 per cent. of compound *a* of 25 per cent. silicon, and 25.6 per cent.

of compound *b* of fifty per cent. silicon. In the first case there is a great excess of the 33.3 per cent. compound, and we might expect that compound *a* could not form well-developed crystals. In the second case compound *a* being far in excess it would probably yield better-developed and larger crystals. I have pulverized the alloy of 31.4 per cent. silicon, to forty mesh sieve, and attacked it with such an amount of hydrofluoric acid as is not sufficient to dissolve the whole mass.

If now the first case be true, the compound *a* will be probably more soluble in acids than the other compound, which contains more silicon. This is a general rule among silicides. Compound *a* is only present in small amounts and is probably not present in large, well-developed crystals. The result will be that compound *a* will be quite or nearly dissolved, and some of the compound of 33.3 per cent. silicon will remain in a more or less pure condition. The residue will then contain more silicon than the original alloy.

In the second case there is a chance for a larger percentage of compound *b* than of compound *a* to be dissolved; for although the latter be more soluble in acids, it is present in large excess and probably in much larger and better-developed crystals than the compound *b*. If a larger proportion of compound *b* than of compound *a* should be dissolved, the residue will contain less silicon than the original alloy.

Acting on the coarsely powdered alloy of 31.4 per cent., silicon was found to produce a residue which contained less silicon than the original.

	Original alloy. Per cent.	Residue. Per cent.
Silicon	31.4	30.2

This result renders the presence of a compound FeSi doubtful.

PROPERTIES.

Iron silicides are invariably crystalline, and are white or gray in color. Silicide with from twenty-five to thirty per cent. silicon takes a fine polish, when it more or less resembles silver, although somewhat darker. The higher-grade silicides are the darker in color. The melting-point rises with the percentage of silicon. Silicide of twenty-six per cent. silicon can be melted in the crucible of a brass furnace, but takes a higher temperature than brass. Silicide of thirty-two per cent. silicon cannot be melted that way. This latter can be melted in a crucible by using a good blast. The silicides containing more silicon could be successfully melted only in an electric furnace. These silicides should not be molten in a blast cupola. The silicon burns as easy or easier than the coke, and the molten metal will contain considerably less silicon than the original. A lot sent to a foundry and treated in a cupola lost five per cent. silicon out of twenty-seven per cent. If such partly oxidized metal is cast, it will often form a coating of a gelatinous silica in the mold. The latter is weakly transparent and elastic to quite a degree. I saw similar silica exhibited in the Carborundum Works at Niagara Falls.

Lower-grade silicides cast very well with sharp outlines and corners. When the amount of silicon is increased, the castings show a tendency to crack when cooling. The silicides of thirty-four to forty per cent. silicon usually form blowholes besides cracking, when the castings cool. When the higher-grade silicides are cooled very slowly the tendency to crack is lessened. All these silicides are but slightly magnetic, and those with over thirty per cent. silicon are quite non-magnetic, which well shows that there is no free iron in the alloy. Their specific gravity falls with the percentage of silicon.

	Alloy of 12 per cent. silicon.	Alloy of 25 per cent. silicon.	Alloy of 46 per cent. silicon.
Specific gravity at 20° C.	6.8	6.36	4.85

These alloys conduct electricity easily, and are very hard. They are brittle, the more so when the percentage of silicon increases. They are unalterable in air or in water. Acids attack them very little, especially if they are not pulverized. Hydrofluoric acid forms an exception, for it easily dissolves all these alloys. Acid oxidizing agents attack these silicides less, the more silicon there is present. In order to obtain some idea of the rate at which the solubility in these agents varies with the percentage of silicon, three samples, *a*, *b*, and *c*, were ground so that they easily pass through a 100-mesh sieve. Two grams of each were treated with the reagent at summer temperature, side by side for two days, stirring frequently.

	50 cc. aqua regia $1HNO_3$ to $3HCl$. Per cent. dissolved.	100 cc. saturated chlorine water. Per cent. dissolved.
a with 13 per cent. silicon	66.84	5.88
b " 25 " " "	9.86	....
c " 46 " " "	0.76	0.83

Toward alkalies the low grades are more resistant than the high grades. Fifty cc. of a twenty per cent. solution of caustic soda dissolved in two days from two grams of the ground silicide:

a with 13 per cent. silicon,	3.96	per cent. dissolved.
c " 46 " " "	9.68	" " "

Silicides made at Holcomb Rock contained:

	I. Per cent.	II. Per cent.
Silicon	26.35	36.56
Manganese	trace	0.31
Sulphur	trace	trace
Phosphorus	trace	trace
Titanium	....	0.94
Carbon	none	none

This alloy is thus shown to be of great purity.

Pieces of iron silicide are often found in calcium carbide, especially in carbide made from inferior materials. I found in such pieces from twelve to forty-five per cent. silicon. Any attempt to write chemical formulas for the material of such pieces must fail. They are mixtures of the same nature as those obtained in quantity.

MANUFACTURE.

The raw materials, which are commonly used in the works of the Willson Aluminum Co., are a good iron ore, river sand, and any kind of coke. The river sand contains some manganese and titanium. The quality of the iron ore can be materially reduced so long as the chief impurity is silica. In fact, for many reasons such an ore is preferable. After trying many fluxes, they were entirely abandoned, for they always reduce the output.

The materials are finely ground with the exception of the silica which should be of the size of coarse sand, on account of its volatilizing easily; and being very light, it is readily carried away by the draft of the furnace. At the temperature that exists in the electric furnace, the carbon monoxide does not act as a reducing agent, and it is the solid coke particles that do the reducing. For this reason the mixing must be thorough and the ingredients must be finely ground.

We use at Holcomb Rock Works a continuous furnace of my own design. It is fed at the top and tapped at the bottom. These furnaces are run one week or in fact any length of time, and they can be cleaned and made ready for use again in a few hours. We make, so far, iron silicide in furnaces of only about 150 electrical horse-power, but by enlarging the furnace, we can easily use 1000 horse-power or more in one furnace, which will materially reduce the cost. Our furnaces give little dust and that only when they are opened. This is a great advantage, for the fine silica dust is very objectionable. I have seen this dust settle two inches deep all over the room from an open furnace.

During the operation the alloy runs to the bottom of the furnace, where it collects in a pool and is tapped at regular intervals. There is only little slag, if the materials are mixed in proper proportions. The metal which runs out is very free of enclosed slag. It comes out white and the tapping can be seen for quite a distance if windows or doors of the factory are left open. An excess of silica must always be taken, to make up for that which volatilizes. This excess must be materially increased when the higher-grade alloys are to be prepared. Since this volatilization of silica requires power, it follows that it takes more power in proportion to make a high-grade than to make a low-grade silicide. We use about twice as much power to make an alloy of thirty-five per cent. as to make one of twenty-five to twenty-seven per cent. The silicon in the former alloy is correspondingly more expensive.

USES.

On account of their great purity and small bulk these silicides are superior to those made in the blast-furnace, but they can only be used instead, where the character of the work admits of paying a larger price for the unit of silicon.

These alloys are very resistant against acid oxidizing agents and conduct electricity well. They are a cheap material for anodes for electrolysis in aqueous baths. The lower grades make nice correct castings. We exhibited, in Atlanta, in 1895, some articles cast from a twenty-five per cent. alloy. These low-grade alloys can be used for making luxury articles, statuettes, etc. The metal when polished has a beautiful, and lasting luster. The higher grades and also the lower grades may perhaps be used instead of aluminum in the heating process of Goldschmidt. This process consists of mixing aluminum foil with some substance capable of yielding oxygen, and igniting the mixture at one point. The reaction between the aluminum and the oxygen, if started at one point, gradually proceeds through the whole mass and a heat is produced, which, in intensity, is second only to that of the electric arc. The silicon of the iron silicide may replace the aluminum, and can be made for a lower figure. These silicides are valuable abrasives, being very hard, and still easily crushed.

WILLSON ALUMINUM CO.,
HOLCOMB ROCK, VA.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN.]

PERHALIDES OF QUINOLINE.[1]

BY P. F. TROWBRIDGE.

Received December 13, 1898.

THE most of the work reported in this paper was completed in the spring of 1897. Publication was delayed because the author hoped soon to be able to complete the study of the halogen salts of quinoline, and the action of the halogens upon these salts and upon the base itself. Other duties have prevented this until it is deemed advisable to present the work in so far as ready, hoping to continue the research during the following year.

The halogen salts of quinoline have been known for a long time, yet only the chloride[2] seems to have been reported. No attempt was made to prepare this salt in crystalline form. For the experiments where the chloride was used it was assumed that it was formed by the addition of an excess of hydrochloric acid to the base. The results confirm this assumption.

An attempt was made to prepare the quinoline hydrobromide in pure condition. A mixture of the acid and base was warmed

[1] Continuation of previous paper. This JOURNAL, 19, 558.

[2] Schiff: *Ann. Chem.* (Liebig), 131, 112.

for some time on the water-bath. Upon cooling, nearly colorless needle-like crystals were obtained. As these were found to be exceedingly deliquescent, and the chief object in the preparation being the study of the further action of the halogens, the attempt at analysis was deferred. (This salt will be investigated later.)

Quinoline Hydriodide, $C_9H_7N.HI$.—Hydriodic acid (boiling-point 126°–127°) was added in slight excess to quinoline, and the mixture heated over a small flame in a flask provided with a reflux condenser. Upon cooling, the iodide separated out as yellow needle-shaped crystals. They were recrystallized from absolute alcohol. Melting-point 135°.

	Calculated for $C_9H_7N.HI$.	Found. I.	Found. II.
Iodine	49.39	49.44	49.32

Quinoline Methyl Chloride, $C_9H_7N.CH_3Cl$, has been prepared[1] by heating quinoline, methyl alcohol, and concentrated hydrochloric acid to 160° for ten hours. Perfectly white crystals containing one molecule of water were obtained melting at 126°, and at 140° losing water and becoming deliquescent and rosy red. That used in the following experiments was prepared, without attempt at crystallization, by shaking a watery solution of quinoline methyl iodide with freshly precipitated silver chloride.

Quinoline Methyl Bromide, $C_9H_7N.CH_3Br$, was prepared by passing methyl bromide into quinoline. An abundance of colorless needle-like crystals were obtained. They were dried and used directly in the following experiments. They are readily soluble in water, alcohol, ether, and chloroform ; slightly soluble in acetone, and almost insoluble in petroleum ether and benzene. Melting-point 70°. (Analytical data and other properties will be given in a later paper.)

Quinoline Methyl Iodide, $C_9H_7N.CH_3I$, has been reported by Williams[2] and La Coste.[3] For the following experiments it was prepared by heating quinoline and methyl iodide, on a water-bath, in a flask provided with a reflux condenser. They are sulphur-yellow crystals, soluble in water, alcohol, chloroform,

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[1] Ostermayer : *Ber. d. chem. Ges.*, 18, 593.

[2] *Jsb. d. Chem.*, *1856*, 534.

[3] *Ber. d. chem. Ges.*, 15, 192.

and ether Melting-point 72°, agreeing with Williams and LaCoste.

Quinoline Hydrobromide Tetrabromide, $C_9H_7N.HBr.Br_4$.—Hydrobromic acid was added, in slight excess, to quinoline, and the mixture then saturated with the vapor of pure bromine. A heavy, dark, oily layer separated, which soon solidified as a mass of dark red cubic crystals. They are soluble apparently without decomposition in water, ether, alcohol, and chloroform. Upon exposure to the air they gradually decompose, bromine being given off. Melting-point 39°.

	Calculated for $C_9H_7N.HBr.Br_4$.	Found. I.	II.
Total bromine	75.42	75.23	75.10
Bromine by thiosulphate	60.34	60.61	60.69

A portion of the crystals above described was exposed to the air until constant weight was obtained and no more bromine seemed to be evolved. The compound was then easily soluble in water, alcohol, ether, and chloroform. It crystallized from the last as beautiful red needles, apparently perfectly uniform in composition. Melting-point 88°. Analysis shows it to be a mixture of lower perbromides, and not a definite compound.

Quinoline Hydrobromide Dibromide, $C_9H_7N.HBr.Br_2$.—When an aqueous solution of quinoline hydrochloride was saturated with bromine, a heavy, red oil settled to the bottom, becoming a solid mass of red crystals as soon as separated from the supernatant liquid and exposed to the air. These crystals were dried rapidly between filter-papers and recrystallized from chloroform, fine red crystals melting at 98°–99°. A qualitative test showed entire absence of chlorine.

	Calculated for $C_9H_7N.HBr.Br_2$.	Found. I.	II.
Bromine by thiosulphate	43.20	43.07	43.10
Total bromine	64.80	64.29	63.98

Quinoline Methyl Bromide Dibromide, $C_9H_7N.CH_3Br.Br_2$.—Crystals of quinoline methyl bromide were dissolved in water and the solution saturated with bromine. At first a yellow precipitate formed, gradually changing to a heavy, red oil. When the oil was exposed to the air for the evaporation of the excess of bromine, it became a very hard, yellow, crystalline mass, almost insoluble in water and ether, sparingly soluble in chloroform, and readily soluble in absolute alcohol, from which it crystallizes as yellow needles. Melting-point 108°

	Calculated for $C_9H_7N.CH_3Br.Br_2$.	Found.		
		I.	II.	III.
Bromine by thiosulphate...	41.39	41.81	41.75	41.72
Total bromine	62.44	62.42	62.35	....

Quinoline Hydriodide Tetraiodide, $C_9H_7N.HI.I_4$.—Fifteen grams of iodine, dissolved in alcohol, were mixed with five grams of quinoline hydriodide, dissolved in water. Upon standing for some time a large bulk of black crystals was obtained. These were found to crystallize best from about sixty per cent. alcohol, from which solution they were obtained as lustrous black plates. Melting-point 76°.

	Calculated for $C_9H_7N.HI.I_4$.	Found.	
		I.	II.
Iodine by thiosulphate.......	66.36	66.37	....
Total iodine	82.95	82.60	82.87

This same compound was formed when an alcoholic solution of iodine was added in excess to a solution of quinoline hydrobromide. The crystals first obtained were twice recrystallized from alcohol. Melting-point 76°. A qualitative test showed entire absence of bromine.

	Calculated for $C_9H_7N.HI.I_4$.	Found.	
		I.	II.
Iodine by thiosulphate	66.36	66.31	66.33
Total iodine	82.95	82.51	....

Quinoline Methyl Iodide Tetraiodide, $C_9H_7N.CH_3I.I_4$.—An excess of an alcoholic solution of iodine was added to an aqueous solution of quinoline methyl iodide, $C_9H_7N.CH_3I$. Crystals began to form immediately and after a short time were separated from the mother-liquor, dried, and twice recrystallized from alcohol. Melting-point 70°. Analyses I and II are given below.

In another preparation, an alcoholic solution of iodine was added in excess to an aqueous solution of quinoline methyl chloride. Very dark crystals soon formed, which were dried and twice recrystallized from absolute alcohol. A qualitative test showed absence of chlorine, but the analytical results are a little high for the pure quinoline methyl iodide tetraiodide,— III and IV below.

In still another preparation, an alcoholic solution of iodine was added, in excess, to an aqueous solution of quinoline methyl bromide. Crystals began to form at once. After standing for some time the crystals were drained, dried, and recrystallized from alcohol, forming black-green crystals, melting at 70°. A qualitative test showed the absence of bromine,— V and VI below.

	Calculated for	Found.					
	$C_9H_7N.CH_3I.I_4$.	I.	II.	III.	IV.	V.	VI.
Iodine by thiosulphate..	65.15	65.11	65.06	66.81	66.62	65.08	65.06
Total iodine...........	81.45	81.18	81.26	82.93	82.54	....	....

Quinoline Hydrochloride Bromide, $C_9H_7N.HCl.Br$.—Chlorine was passed for three hours into a mixture of quinoline and hydrobromic acid dissolved in an abundance of water. The solution became dark-colored and crystals were formed. Gradually the liquid became clear with a voluminous mass of yellow crystals in the bottom of the dish. These were washed with warm water and twice recrystallized from chloroform. They form fine yellow needles melting at 101°-102°.

	Calculated for	Found.	
	$C_9H_7N.HCl.Br$	I.	II.
Halogens by thiosulphate ...	14.42	14.29	14.27
Total halogens..............	46.97	46.73	46.54

Quinoline Methyl Chloride Bromide, $C_9H_7N.CH_3Cl.Br$.—Quinoline methyl bromide was dissolved in water and saturated with chlorine. A yellow crystalline mass was formed, soluble in chloroform, from which it crystallized as yellow scales. Melting-point 112°. A qualitative test showed the presence of bromine.

	Calculated for	Found.	
	$C_9H_7N.CH_3Cl.Br$.	I.	II.
Halogens by thiosulphate...	11.35	11.10	11.03
Total halogens	32.94	32.17	32.11

Quinoline Hydrochloride Iodochloride, $C_9H_7N.HCl.ICl$.—Quinoline hydriodide dissolved in water, was warmed on the water-bath and then saturated with chlorine. The solution became dark at first, as if from precipitated iodine, then the dark color gradually disappeared with the formation of yellow crystals. These are sparingly soluble in chloroform, but long yellow prismatic crystals were obtained by partial evaporation of the chloroform solution and then setting aside, loosely covered, in a cool place. Melting-point 112°.

	Calculated for $C_9H_7N.HCl.ICl$.	Found. I.	II.
Halogens by thiosulphate ...	21.61	21.75	21.64
Total halogens	60.27	60.04	59.70

Quinoline Methyl Chloride Iodochloride, $C_9H_7N.CH_3Cl.ICl$.—A watery solution of quinoline methyl iodide was heated on the water-bath and saturated with chlorine. The clear solution rapidly assumed a very dark brown color, gradually changing to a clear solution and a yellow precipitate. The precipitate was collected, dried, and recrystallized from chloroform. Fine yellow crystals were obtained.

	Calculated for $C_9H_7N.CH_3Cl.ICl$.	Found. I.	II.
Halogens by thiosulphate ...	20.73	20.60	20.58
Total halogens	57.80	57.64	57.48

Quinoline Hydrobromide Iodobromide, $C_9H_7N.HBr.IBr$.—Quinoline hydriodide was dissolved in water and saturated with bromine. A dark oil, containing crystals, soon settled to the bottom of the liquid. The oily and crystalline mass was carefully separated from the supernatant liquid, and warmed upon the water-bath to drive off excess of bromine. A red crystalline mass was obtained moderately soluble in absolute alcohol, from which solution it crystallizes nicely after partial evaporation. Melting-point 109°.

	Calculated for $C_9H_7N.HBr.IBr$.	Found. I.	II.	III.
Halogens by thiosulphate ...	38.36	38.40	38.31	38.34
Total halogens	68.77	68.52	68.40	....

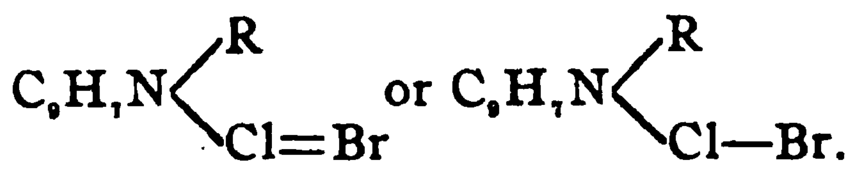
Quinoline Methyl Bromide Iodobromide, $C_9H_7N.CH_3Br.IBr$.—Heavy, dark red oil is formed upon saturating a watery solution of quinoline methyl iodide with bromine. Upon exposing the oil to the air for the evaporation of the excess of bromine, a mass of reddish crystals was obtained. These crystallized from absolute alcohol as yellow plates containing iodine. Melting-point 108°.

	Calculated for $C_9H_7N.CH_3Br.IBr$.	Found. I.	II.	III.
Halogens by thiosulphate ...	37.11	37.66	37.32	37.24
Total halogens	66.51	66.40	66.37	....

SUMMARY.

The action of bromine upon quinoline methyl chloride has not been studied, nor the action of the halogens upon the ethyl halides of quinoline. These will be reported later. Iodine completely displaces chlorine from quinoline hydrochloride, but in all cases a tarry-like mass was obtained, which could not be purified for analysis.

The general reactions with quinoline are very similar to those with pyridine[1]. No perchlorides of the normal chlorides are formed. Chlorine seems to displace bromine and iodine from the normal position, and then, with the iodocompounds, to combine with the displaced halogen, forming iodochlorides of the normal chlorides. With the bromides there is but one atom of perhalogen, thus giving other instances of a probable bivalent halogen[2]; *i.e.*,



$$C_9H_7N\Big\langle\begin{matrix}R\\ Cl{=}Br\end{matrix} \text{ or } C_9H_7N\Big\langle\begin{matrix}R\\ Cl{-}Br.\end{matrix}$$

Bromine displaces chlorine completely, forming perbromides of the normal bromides. It displaces iodine from the normal position and then combines with the displaced iodine to form an iodobromide of a normal bromide. Iodine displaces both chlorine and bromine from the normal position forming periodides of the normal iodides.

The action of the halogens upon quinoline has been studied by Grimaux,[3] Claus and Istel,[4] Ostermayer,[5] and Dittmar[6]; but none of these give the action of reducing agents as showing the probable relation of the halogen atoms. It is purposed to take up this study in the near future.

I wish to express my thanks to Professor A. B. Prescott, in whose laboratory and under whose general supervision the work has progressed; also to Mr. John D. Wombacher, for his assistance in the laboratory at Ann Arbor.

MARBURG, GERMANY, November 24, 1898.

[1] This Journal, 19, 558.

[2] *Ibid.*, 19, 322.

[3] *Bull. Soc. Chim.*, 38, 124

[4] *Ibid.*, 18, 600.

[5] *Ber. d. chem. Ges.*, 15, 824.

[6] *Ibid.*, 18, 1613.

REVIEW.

THIRD INTERNATIONAL CONGRESS OF APPLIED CHEMISTRY.

[Held in Vienna, July 27–August 4, 1898.]

Dr. C. E. Munroe, President of the American Chemical Society:

SIR: I have the honor to submit the following report of my observations as a delegate of the American Chemical Society to the Third International Congress of Applied Chemistry, held in Vienna, July 27 to August 4, 1898.

The president of honor of the congress was Dr. Alexander Bauer, K. K. Hofrath and professor of chemistry in the Imperial Technical High School of Vienna.

The acting president was Dr. Hugo Ritter von Perger, Regierungsrath and professor in the Imperial Technical High School.

The vice-presidents were chosen from the several sections in proportion to their membership. Nearly all the vice-presidents were selected from among the delegates of foreign nations. Our society was represented among the vice-presidents by Prof. W. B. Rising, of the University of California; Dr. F. G. Wiechmann, chief chemist of the American Sugar Refining Co.; and Dr. H. W. Wiley, chief chemist of the U. S. Department of Agriculture. Among other vice-presidents whose names are well known, may be mentioned Professors Fischer, Buchner, Herzfeld, Claassen, Vogel, and von Lippman, of Germany; Moissan, Fernbach, Dupont, and Lindet, of France; Lobry de Bruyn, of Holland; and Piutti and Verdrödi, of Italy. The members of the Austro-Hungarian Cabinet were also made presidents of honor.

A preliminary meeting of the committees and an informal reception to visiting members took place on the evening of July 27th in the Cursalon of the City Park. A concert by a military band and abundant refreshments were offered to the members of the congress on this occasion.

On the 28th of July the general opening of the congress took place in the Aula of the Vienna University.

The opening discourse was given by Prof. Dr. von Perger, as follows:

"Most esteemed gentlemen: As chosen chairman of this select assembly, I have the great honor of opening the Third International Congress of Applied Chemistry. Permit me, before I fulfil this pleasant duty, to express the wish that this association of the most prominent men of science, honored as it is by the presence of illustrious representatives of various governments, may accomplish the grand purpose which has created it in fully as brilliant a manner as at Brussels and Paris, so that it will justify the intentions of those who see in the personal intercourse of the representatives of applied chemistry, in this international association, an important means of furthering common interests.

"Cooperation in work has, as a look into the past will show, always accomplished great ends. I am certain that I need not enumerate examples as proof of this.

"The great thoughts which have irresistibly guided future progress, the thousands of discoveries and inventions which have rendered possible the development of chemical technics, the tedious labors in the laboratory and factory, are as an open book to you who are cooperating in this grand work directed toward the betterment of all, for they represent at least in part your own experiences. A comparison of the present with the past fully guarantees the constantly increasing importance of technical knowledge, and correspondingly the growing reputation of its representatives. It enables us to determine the paths in which our knowledge of material growth proceeds with regularly increasing rapidity, and even now permits us to recognize great problems whose solution is approaching.

"While in the field of the chemical technology of inorganic compounds the raw materials used on the large scale have remained the same, there being added only the preparation of the carbides and rare earths, the methods of production have been amended with great success with reference to rational management and control.

"The application of electrical energy has caused and will, in the future, result in important changes.

"The raw materials of the chemical technology of organic bodies have in numerous branches of the latter hitherto remained the products of the processes of life, and progress has been confined for the most part to a further development of methods, both analytical and practical, apart from the notable improvements in the fermentation industries.

"The triumphs of synthesis have been mostly identified with the chemistry of coal tar and its constituents. They have not only caused a complete revolution in the textile industries, but have also accomplished much in the preparation of valuable medicinal compounds.

"The theory of the constitution of aromatic compounds, which have proved of such value in the technology of dyeing, has not been without influence on other branches of research. The gulf, which existed for many years between compounds of the 'aliphatic' and 'aromatic' series, has been bridged by the discovery of the 'hydrocyclic' compounds.

"The unitarian system represents fully as great an advance as the synthesis of urea (1828) by Wöhler, which marked an epoch in the history of chemistry in that it once for all overthrew the doctrine that life was an essential to the production of organic compounds.

"The separation of optically inactive substances into other substances which are dextro- and laevo-rotatory, which disproved the hypothesis that the, rotatory power of compounds containing carbon is a characteristic proof of their derivation from organized bodies, was but a further result of the knowledge previously acquired.

"Just as Chevreul at the beginning of this century explained the constitution of the fats by his notable investigations on the process of saponification, the results of which have never been questioned, so has Emil Fischer ushered in a new epoch by his illustrious work on the synthesis of the carbohydrates.

"The well-known hydrolysis of starch, the separation of complex molecular compounds into simpler compounds, whose constitution has been determined, the first synthesis of a 'glucoside' by Emil Fischer, the recent experiments of Marchlewsky on the synthesis of sucrose from artificially produced 'levulose' and 'dextrose', all lead directly to the desire to find 'Reversion-reactions,' which will enable us to build up compounds of high molecular weight, whose molecular complex has been approximately determined by Raoult's method.

"The feasibility of such syntheses being assumed, we more closely approach a solution of the question of organization, and the gap which exists between this and the so-called inorganic compounds will be bridged over similarly to that which formerly separated the fatty and aromatic series.

"The reversion-reactions will secure the synthesis of substances, whose production in this manner will be of great economic value, just as the synthesis of alizarin by Graebe and Liebermann has, and as the preparation of synthetic indigo will become, the latter acquiring more and more practical importance every day.

"The outlook with reference to the results of our present knowledge is elevating; it indicates the satisfactory solution of questions which interest not only the chemist, but the national economist, and possibly the philosopher.

"Encouraged by previous successes and having absolute faith in the unchangeable advance of knowledge, we look into the approaching century with the confidence born of successful investigation, the unity of being, the exploration of the synthesis of organic compounds, those complex compounds, whose synthesis will lead to the secret of the organization of life.

"With this view of the future I have ventured to address this most distinguished assembly and with these modest words I may be permitted to open the Third International Congress."

Dr. Bauer addressed the congress briefly after Dr. von Perger had finished. He said:

"Gentlemen: As honorary president of the committee of organization for this meeting I have the great honor to bid you a cordial welcome, and I take advantage of this occasion to express our satisfaction at seeing so many illustrious members in our midst.

"Our program is rather a large one and involves a great many and various subjects. I think the most satisfactory part of it will be shown in the fact that there is always an agreement in human labor between practical work and theoretical investigation.

"If chemistry has not to be the servant of any one art, as Robert Boyle said two hundred years ago, the chemistry of to-day allows us to serve the arts and at the same time and in the same way to devote ourselves to the study of the highest problems of science.

"In the name of the Austrian chemists I thank most sincerely those who have shown their interest in the success of this congress by personally appearing here; also those who have become members of the congress in all parts of the world, but who have been prevented from attending its meetings. If we shall succeed in making this congress a success, it will be due chiefly to the important position which science and industry have taken in our fatherland.

"For this we thank first of all the wise care and thoughtfulness of our most gracious Emperor, and we are most happy, gentlemen, to have you here on the occasion of the celebration of the fiftieth year of his reign. I invite you, therefore, to join with me in crying, 'His Majesty, our most gracious Emperor and Lord, his royal and Imperial Catholic Majesty, Franz Josef First, er lebe hoch! und dreimal hoch!'"

All the members arose and joined in the cheers, and thereafter the following telegram was sent to the Emperor:

"*To His Excellency, Count Paar,*
"*Chief Adjutant of His Majesty, Ischl.*

"The Third International Congress of Applied Chemistry, now sitting in Vienna, begs your Excellency to present to His Majesty in the name of the Congress the request that His Supreme Majesty will most graciously accept the homage and the most cordial wishes of the Congress on this jubilee year.

"For the Congress: RITTER VON PERGER."

To this telegram the following reply was received:

"In accordance with the imperial command I have the honor to return to the honored chairman of the Third International Congress of Applied Chemistry the thanks of the Emperor for the telegram of homage addressed to His Imperial and Royal Apostolic Majesty.

"KUENBURG.

"Ischl, July 29, 1898. "Acting for Count Paar."

Dr. Strohmer, the general secretary of the Congress, then presented his preliminary report, in which the organization of the work of the congress was discussed. Committees on organization were formed by the central committee, not only in Austria, but also in other countries. The Austrian committee consisted of nearly 200 persons, of whom 153 were inhabitants of Vienna. 12,000 circulars were printed in German, French, and English, and sent to chemists in all parts of the world. Notices of the meeting were printed in more than 200 scientific journals. Special invitations were sent to more than 600 investigators in all countries to prepare papers, and the hundreds of responses received show how generally these invitations were accepted. In closing, Prof. Ströhmer said:

"In this short report I hope I have shown that the organization committee of the Third International Congress of Applied Chemistry has not in earnestness and industry fallen behind the Paris committee for the second congress, and I further hope, gentlemen, that you will find that we have laid a sufficient foundation for your work while here."

SCIENTIFIC ADDRESS BEFORE THE WHOLE CONGRESS.

Only one scientific address was delivered before the general session of the congress; *viz.*, "Fermentation without Cells," by Prof. Buchner. The speaker stated that the results he had obtained, and which he would proceed to demonstrate, showed that the old notion which supposed that fermentation could only take place under the influence of a living cell, like that of yeast, for example, was evidently erroneous. Cells capable of effecting fermentation probably acted through the production of another body, a residue of cell vitality, and it was this body that was the active principle. The method of preparing yeast liquor containing no yeast cells was described in detail. Fresh Munich beer yeast is deprived of water by a pressure of fifty atmospheres, and is then mixed with an equal weight of quartz sand and a fifth of its weight of kieselguhr, and the whole pulverized. The process is continued until the pulverized mass begins to stick together and on examination with the microscope shows that at that time about forty per cent. of the yeast cells are crushed. The mass is placed on a cloth and gradually subjected to a pressure of 500 atmospheres in a hydraulic press. The cake is removed, moistened with water, and again pressed.

From one kilo of yeast about 500 cc. of juice are obtained by the above treatment, of which only about 140 cc. should be due to the added water. The expressed yeast juice drops from the press into a folded filter, and the filtrate is received in a flask cooled with ice-water. Nearly all the yeast cells are destroyed by the pressure, the microscope showing only about four per cent. intact. The others are seen to be only empty walls, their contents having all been expressed. In the yeast juice certain enzymes are found; *viz.*, invertose, oxydases, and proteolytic ferments. The yeast juice is capable of fermenting sucrose, maltose, *d*-galactose, *d*-fructose, *l*-arabinose, and mannose. It does not act on lactose. *d*-Galactose and glycogen are fermented with difficulty.

It appears, therefore, that fermentation is not a physiological process, or, in other words, a complex vital act. It depends rather on an enzyme-like body resembling zymose, which is produced only in the organisms of living cells like those of yeast. Numerous experiments, showing the fermentative action of the yeast juice, were made during the progress of the lecture.

THE WORK OF THE SECTIONS.

The congress, after the opening session and the address of Prof. Buchner, separated into sections, of which twelve were organized for work. On account of the large number of papers offered in some of the sections, it was found necessary to organize a number of subsections. The final arrangement for sectional work was as follows:

Sec. I. General analytical chemistry and apparatus.
" *II.* Medical, pharmaceutical, and food chemistry.
  Subsection A. Pharmaceutical chemistry.
  " B. Food chemistry.
  " C. Medical chemistry.
" *III.* Agricultural chemistry.
" *IV.* Chemistry of the sugar industry, starch and grape sugar.
" *V.* Chemistry of fermentation.
  Subsection A. Beer brewing and malt manufacture.
  " B. Alcohol and compressed yeast industry.
" *VI.* Chemistry of wine.
" *VII.* Chemical industries of inorganic materials.
" *VIII.* Metallurgy, mining chemistry, and explosives.
" *IX.* Chemical industries of organic bodies.
  Subsection A. Coal-tars and textile dyes.
  " B. " " " " "
  " C. Chemistry of fats, oils, and lubricants.

Sec. IX. Subsection D. Paper and cellulose.
" E. Tanning and glue.
" *X.* Chemistry of printing (lithograph, photograph, etc.).
" *XI.* Didactic chemistry.
" *XII.* Electrochemistry.

It would not be possible to give an extract or even the titles of the hundreds of papers read before the sections. Unfortunately, no complete programs of the papers read before each section were printed, and members could only find out what was going on by going from section to section. Only brief abstracts, and of these only of the most important papers, were printed during the congress. A rather comprehensive résumé of the papers presented is appearing in the *Oesterreichische Chemiker-Zeitung*, in the *Chemiker-Zeitung* edited by Dr. Krause at Cöthen, and in the *Wockenschrift des Central-vereins für Rübenzucker Industrie in der Oesterr-Ungarische Monarchie.* Practically all the papers will appear in full, in the various chemical journals, and in the printed proceedings of the Congress.

Some of the more important papers presented in the various sections are as follows:

Sec. I.—1. Estimation of Phosphoric Acid, by Prof. H. Lasne.

2. Choice of Atomic Weights, by Dr. Bersch.

3. Proposals for the Uniform Use of Indicators in Volumetric Analysis, by Dr. Paul Degener.

4. Final action on the resolutions of the Second International Congress relating to the construction and introduction of uniform areometers, burettes, etc.

Sec. II.—1. Testing Butter for Foreign Fats and Refractometric Milk Analysis, by Dr. Wollny. In these papers Dr. Wollny described the use of his refractometer for determining the fat in the ether extract of milk obtained in much the same way as in the old Soxhlet method of determining the fat by the density of the ether solution. The method is very rapid and reasonably accurate, and especially where small quantities of fat are concerned, as in the case of skim milk.

2. Examination of Lard, by Dr. Raumer.

3. Examination of Ethereal Oils with the Polariscope, by Dr. Duyk.

4. Determination of the Purity and Activity of Serum, by the French Committee.

5. Determination of Gluten in Flours, by M. Fleurent.

6. Changes of Chlorine-holding Materials in the Organism, by Dr. Gross.

7. Analysis of Potable Waters, by M. Durand.

8. Is It Possible to Detect Pure Brandy by Chemical Means? by Dr. Werber.

9. What is the Limit of Copper Content in Preserved Vegetables, etc., by Dr. Baum.

10. Synthesis of Protein, by Dr. Leon Lilienfeld.

Sec. III.—1. Plants Suitable for Cultivation on Forest Domains, by Arthur Thezarie.

2. Culture of Peaty Lands, by Dr. B. Tacke.

3. Rational Treatment of Stall Manures in Order to Avoid Loss of Nitrogen, by Dr. Schneidewind.

4. The Chemical Composition of Indian Corn and Its Important Products, by Dr. H. W. Wiley.

5. Feeding Cattle with Molasses, by M. Vivier.

6. Unification of Methods for the Analysis of Chemical Manures, by Prof. Angelo Menozzi.

7. Determination of Phosphorus Pentoxide as a Control Method, by Dr. Ritter von Grueber.

Sec. IV.—1. The Role of Pentosans in Sugar Manufacture, by Dr. A. Stift.

2. Influence of Saccharose on the Determination of Pentosans, by Karl Andrlik.

3. Influence of Temperature on the Specific Rotatory Power of Sucrose, by H. W. Wiley.

4. New Processes of Sugar Manufacture and Increased Output, by Dr. A. Herzfeld.

5. The Electrolytic Estimation of Sugar, by J. Formanck.

6. Crystallization of Amorphous Sucrose, by F. G. Wiechmann.

7. Greek Sugar Beets, by Prof. A. Christomonas.

8. The Chemical Nature of Caramel, by N. Fradniss.

9. The Viscosity of Sirup, by Dr. A. Classen.

10. International Methods of Determining the Quality of Sugarbeet Seed, by G. Pammer.

Sec. V.—1. The Diastatic Power of Mushrooms, by Dr. Jean Effront.

2. International Agreement of Methods of Malt Examination, by Prof. L. Aubry.

3. The Steps in the Hydrolysis of Starch, by Prof. Dr. Lintner.

4. The Pasteurization of Beer in Bottles and Barrels, by Prof. Caro.

5. Continuous Rectification, by Drs. Barbet and Fernbach.

6. Estimation of Aldehydes, by Prof. Istrati.

7. Invert Sugar Estimation, by Dr. G. Bruhus.

Sec. VI.—1. Methods for the Chemical Examination of Wine, report by Drs. Barth, Bain, Kruger, and Haas.

2. Influence of Climatic Conditions on the Wine, by Dr. Radulescu, Prof. Dr. Hilger, and Dr. Roesler.

3. Influence of Animal and Plant Parasites on the Character of the Wine, by Prof. Barth.

4. Influence of Fertilization on the Character of the Wine, by Prof. Barth.

5. Influence of the Different Ferments on the Character of the Wine, by Prof. Worthmann.

6. Methods of Controlling the Progress of Fermentation, by Dr. Joseph Bersch and W. Seifert.

7. Influence of the Electric Current on the Ripening of Wine, by Drs. Barth and Kreps.

Sec. VII.—1. The Present Condition of the Petroleum Industry, by Prof. Zalozucki.

2. The Flashing-point of Petroleum, by C. A. Lobry de Bruyn.

3. Acetylene Generators and Acetylene Burners, by Dr. N. Caro.

4. The Industrial Manufacture of Ammonium Nitrate, by M. Truchot.

5. Chemical Processes in the Burning and Slaking of Lime, by Prof. Dr. A. Herzfeld.

Sec. VIII.—1. The Manufacture of By-products from Iron Ores, by Emil Hulz.

2. International Agreement with Reference to the Handling and Transport of Explosives, by Phillip Hess and Julius Ephriam.

3. Theory of Safety Explosives, by Julius Ephriam.

4. Chemical and Microscopic Examination of Gunpowder, by A. Croquert.

5. A New Process of Producing Water-gas, by George Hangsdorf.

6. Some New Methods of Steel Analysis, by L. Verrier.

7. New Methods of Electrical Estimation of Zinc in Ores, by Dr. Henry Pawck.

Sec. IX.—1. The Present Condition of the Chemistry of Coal-tars, by Dr. P. Friedländer.

2. International Adoption of the Baumé Scale for the Determination of Specific Gravity, by Prof. Wolfbauer.

3. The Analysis of Resins, by Dr. Carl Dietrich.

4. The Technical Analysis of Bone Fats, by Dr. Slenkoff.

5. The Chemistry of Paper-making, by Dr. Kellner.

6. The Analysis of Tanning Substances, by Prof. Müller.

7. Study of the Different Kinds of Glues, by A. Cronquist.

Sec. X.—1. Influence of the Chemical Composition of Glass on the Character of Photographic Lenses, by Dr. A. Miethe.

2. Results of Experience in Photographing with Artificial Lights (Magnesium, Aluminum, Auer, Acetylene, etc.), by Henry Kessler.

3. Methods for Determining the Precious Metals in Photographic Baths, by Prof. A. Lainer.

4. Best Methods of Recovering the Precious Metals from Photographic Residues, by Prof. A. Lainer.

5. Most Sensitive Paper for the Less Refracted Spectral Rays, by Dr. M. Andresen.

Sec. XI.—1. The Education and Qualifications of Official Food Chemists, by Dr. Kaiser.

2. The Requirements for Official Technical Chemical Service in Austria-Hungary, by Dr. N. Bomburger.

Sec. XII.—1. Preparation and Properties of Metallic Calcium, by Prof. H. Moissan.

2. Novelties in Eletrochemical Technics, by Dr. Kellner.

3. Uniform Conditions in Electrochemical Work, by Dr. G. Vortmann.

REMARKS ON PAPERS.

In addition to the papers already mentioned, those by Moissan and Lilienfeld attracted general attention. American chemists are so familiar with Moissan's work that it would be a work of supererogation to refer to it here at any length. The methods of preparing metallic calcium were described, samples of the metal shown, and its physical and chemical properties illustrated.

ARTIFICIAL ALBUMEN.

The synthesis of a peptone or peptonoid by Lilienfeld marks a distinct step forward in synthetic work, in the field already partly explored by Grimaux, Pickering, Williamson, and others. We can now speak, however, only of its centesimal composition. The state of its molecular condensation and atom position can only be determined by securing large quantities of the product and submitting it to chemical and digestive studies. It is probable that, as in the case of sugars, the artificial peptone will lack the vital element. In other words, while the chemist has succeeded in building molecules which resemble, in every outward respect, those built up by nature, they are uniformly dead, without cell functions or cell activity. The details of this important scientific work must be awaited before a final judgment, in regard to its far-reaching importance, can be formulated.

The synthesis of peptone is effected by the condensation of phenol with glycocoll with the help of phosphoroxychlorid. A hydrochlorate of peptone results, which gives all the characteristic reactions of protein. By conversion into sulphate and the decomposition of the latter, the free peptone is obtained which, it is claimed by Lilienfeld, is similar both in chemical and physiological properties to the natural product.

It is evident from the method of preparation that the product contained no sulphur, since the only sulphur-containing ingredient used was sulphuric acid, and this could not possibly enter into the organic preparation. Granting that a peptonoid body was produced, the synthesis of a true proteid, which should contain sulphur, is still undemonstrated.

The color reactions which are supposed to be characteristic of protein must not be relied on too surely. They are probably due to decomposition, and not to the action of the molecule as a whole. It is stated by Pickering that a mixture of tyrosin, indol, and biuret will give all the reactions characteristic of a proteid. If the prospects of artificial food depended on these so-called synthetic products, the vocation of the geoponist would be assured for many millions of years to come.

PAPERS BY AMERICAN CHEMISTS.

There were only a few papers presented by American chemists. Dr. Wiechmann read a paper on "The Crystallization of Amorphous Saccharose." It was shown that the presence of invert sugar, the intensity of light, and, in an indirect manner, the presence of certain inorganic salts, influenced the beginning and progress of crystallization. As a result of the investigation, it was established:

1. That the crystallization of amorphous sucrose is to be ascribed to the presence of crystals of ordinary sucrose which are contained in the melt.
2. The change of amorphous into crystallizable sucrose is hindered by the presence of invert sugar, and the retardation is proportional to the amount present.
3. Inorganic salts and certain other bodies do not, of themselves, tend to produce crystallization of the amorphous sucrose.
4. Alkaline salts which tend to prevent the inversion of sucrose, and thus keep the proportion of invert sugar down, favor a condition which results in the more rapid crystallization of the amorphous sucrose.
5. Light, or the energy produced thereby, favors the crystallization.

In introducing the paper the author referred to his previous publication on the subject, in which the methods of preparing amorphous sucrose were described.

Dr. Wyatt's paper on "American Methods of Fermentation" was listened to with great interest, especially by those who supposed that no information on this theme could come from America.

Dr. Wyatt divided the subject of fermentation into two classes; *viz.*, sugars readily fermentable, and sugars and non-sugars which do not readily ferment or which are necessary to give roundness or mellowness to beer. If the sugars of these two classes really exist as separate compounds, they may be regarded as malto-dextrin. In addition to these the brewer must also consider the dextrins which are quite unfermentable, and yet which give body to beer. The free acidity of beers is due chiefly to phosphoric and lactic acids. A barrel of beer of ordinary composition weighs 171 pounds and contains 35.4 pounds of solid matter. The total free acid estimated, as lactic acid in a barrel of beer is 0.406 of a pound, or 0.15 per cent. Normal beer yeasts require slightly acid pabulum, while the foreign organisms found in breweries, and which cause so much trouble, flourish best in neutral or alkaline fluids. Acidity also causes various types of albumens to remain in solution in the beers. The poor flavor characteristic of pasteurized beers is mainly attributable to their lack of acidity. The mineral matters in beer are chiefly phosphates, together with some sulphates or chlorides. All the acids are chiefly in combination with potassium and lime. The nitrogenous bodies which are in solution in beer belong to the classes of albumoses, peptones, and amids. As the temperature of beer decreases, portions of these bodies tend to be precipitated, and thus a beer which is brilliant at a temperature of 50° will become cloudy if the temperature is decreased. It is important, therefore, in the storage of beers, that they be kept at a low temperature long enough to secure a complete precipitation of these bodies. The necessity for a longer cold storage of the beers is not easily established, and the prevailing opinion that they should be kept for a much longer period is probably erroneous.

Dr. Wiley's paper on "The Influence of Temperature on the Specific Rotation of Sucrose" was discussed at length by Drs. Herzfeld and von Lippmann. The methods of research employed were described in detail, and all the disturbing forces discussed and the degree of disturbance determined for each. It was shown that on using a compensating quartz wedge to determine the degree of the rotation the temperature influenced the results obtained in the following ways:

1. It causes a change in the rotatory power of the quartz wedge, this power increasing with a rising temperature. From this it follows that a less thickness of the wedge is necessary to produce a given compensation at a high temperature.

2. The volume of the flask increases with a rising temperature, and hence the volume of the solution is greater as the temperature rises.

3. The weight of water in a given volume decreases as the temperature rises, and hence arise differences in the concentration of the solution.

4. The length of the observation tube increases with a rising temperature.

5. The degree of concentration of the solution affects its specific rotatory power.

6. Any variations in specific rotatory power, which are observed after introducing the correction for the disturbances above noted, must be due to direct effect of the change of temperature on the specific rotatory power.

7. Making the corrections noted, it was found that the specific rotatory power of pure sucrose at different temperatures is as follows:

At 4° α D = 66.653°.
" 17.5° " = 66.547°.
" 40° " = 66.340°.

In his paper on "The Composition of Indian Corn and Its Chief Products," Dr. Wiley discussed the problem of the economic use of maize as food for man and beast. The composition of all parts of the plant was given from the latest analyses, chiefly those of the Chemical Division of the Department of Agriculture. Statistics were given, showing the magnitude and value of the crop in the United States. The extended use of maize as human food in the United States was referred to, and especially the fact that the hard labor of the southern part of the country was done chiefly on a diet of maize bread.

The utilization of the maize stalks as a cattle food, and of the pith as a packing for coffer-dams of battleships and for other purposes, was discussed. The employment of maize as a source of starch, glucose, alcohol, and whisky was described. The chief object of the paper was to call the attention of European scientists to the value of maize for the purposes mentioned, and to show the groundlessness of the prevalent notion in Europe that it is unfit for European consumption. At the close of the paper the prevailing opinion in Europe concerning maize was pointedly brought out by the following question: "Is it true that maize is actually used in your country for bread-making without admixture with the flour of some other cereal?"

The poor opinion which Europeans have of the character of maize bread arises partly from ignorance, and partly from the fact that European maize lacks that delicacy of flavor and richness of taste which belong to the American article. Further than this, it may be mentioned that maize bears, very poorly, transportation across the sea, and therefore the imported maize or maize flour often makes a very unpalatable bread. A method of transporting the maize and preserving it entirely fresh at the same time will do much to remove the unreasonable prejudice prevalent in Europe against maize as a human food.

ATTENDANCE.

According to the report of the general secretary, Dr. Ströhmer, read at the final general session, the membership of the congress exceeded 1,700. The actual attendance, however, fell far short of this number. A great many chemists who took membership tickets did not attend the congress. No list of members actually present was published, and therefore only an estimate not very reliable can be made. Such an estimate would place the actual members in attendance at about 800.

The organizers of this congress should have attended a meeting of the American Association for the Advancement of Science before the opening of the Vienna congress. There was no official program of papers nor list of members published. This part of the work was committed to the publishers of the *Oesterreichische Chemiker-Zeitung*. The result was that no one could find out, except by an accidental meeting, who were in actual attendance. No attempt was made to give the city address of those present, and therefore, except by the aid of the police, the search for a friend was hopeless. These facts are not stated as a carping criticism of the management. On the contrary, the local committee displayed the most commendable zeal n its efforts to entertain and oblige visiting members. About thirty American chemists had taken membership tickets in the congress, but only the following Americans were actually present at the meetings: Prof. W. B. Rising, delegate from the University of California; Dr. J. M. Flint, delegate from the Navy Department; Dr. H. W. Wiley, delegate from the Department of State, the Department of Agriculture, and from the American Chemical Society; Dr. Francis Wyatt, of New York; Dr. F. G. Wiechmann, of New York; Mr. Waldron Shapleigh and Mr. H. C. Watts, of Philadelphia; and Mr. M. Ikuta, of the University of Chicago.

Of other foreign countries, France had the largest representation, the French group consisting of about sixty persons. The Germans, strange to say, were no more numerous than the French. Next in numbers came the Russian contingent, while from the other continental nations only a few representatives were present. As was the case at Paris, England had no representative. The abstention of the English chemists from these congresses is somewhat surprising. Greece was not without a delegate, and it seems somewhat strange to hear a fellow countryman of Homer and Socrates discussing the relative merits of the several varieties of sugar-beets.

PLACE OF NEXT MEETING.

There was practically no opposition to the invitation received from the French delegates to hold the fourth congress in Paris. The Germans, however, have a tacit expression of preference for the congress to go to Berlin in 1902. Since all the world will make a pilgrimage to Paris in 1900, it was almost the unanimous opinion of the delegates that it would not be wise to attempt to hold the next meeting in any other city. In view of the fact that there will doubtless be a large attendance of American chemists at Paris in 1900, the suggestion of the propriety of arranging for their entertainment may not be amiss. If 300 members, or even a less number, of the society propose to attend this congress, it would be conducive to economy and comfort to arrange for quarters in advance. It is therefore suggested that those proposing to attend take concerted action for the purpose of securing proper accommodations. A Congress-Chemical-Exposition Club would, if strong enough in numbers, be able to secure great economy in transportation and entertainment.

PERMANENT COMMITTEE.

Heretofore each congress has been an independent body with a life of its own which has expired with the final adjournment. It was deemed wise at Vienna to make the congress a continuous body, remaining under the constant control of delegates from all represented countries. Dr. Ritter von Grueber proposed, therefore, at the final session, that such a committee be formed, and this proposal was unanimously approved. Some of the members of the committee appointed at this session are named below:

President: Prof. Moissan, of Paris; America: Doremus, Rising, Wiechmann, and Wiley; Austria-Hungary: Meissl, Ströhmer, and von Perger; Belgium: Masson; Denmark: Kjeldahl; England: Procter; France: Berthelot, Déhérain, Dupont, Lasne, Lindet, and Pellet; Germany: Delbrück, Fischer, Herzfeld, and Von Grueber; Italy: Piutti and Verdrödi.

The representatives from other countries will be appointed later by the president of the committee on suggestions from leading chemists and associations of the countries interested. The committee also has power to add to its members in the countries above named.

SECOND MEETING OF THE INTERNATIONAL COMMISSION ON UNIFORM METHODS OF SUGAR ANALYSIS.

This meeting was held on July 31st, in the hall of the Central Association of the Beet-sugar Union of the Austro-Hungarian Monarchy. The chairman of the committee, Prof. Dr. Herzfeld, presided. In all about thirty members were present, among whom may be mentioned Messrs. Dupont and Weisberg, of France; Ströhmer and Stift, of Austria; Weinstein, Thiele, Müller, and Huck, of Germany; Van Ekenstein, of Holland; Nasini, of Italy; and Wiechmann and Wiley, of America.

The chairman of the committee gave a detailed account of the origin of the committee and its first meeting, which was held in Hamburg. He noted with pleasure that in almost all countries which are interested in the sugar industry a desire had been shown to take part in the labors of the commission. Only English chemists have refrained from taking any part in the work of the committee.

Afterwards the chairman gave a detailed account of the international testing of quartz plates. Twenty different plates had been sent to chemists in different parts of the world. The returns were rather incomplete, only seven chemists outside of the laboratory in Berlin having reported results. The results as far as reported show quite a remarkable agreement, in general, in the values obtained. In some instances, however, considerable variations were noted. The chairman stated that the work would be continued during the coming two years with more care, and, if possible, with a greater number of chemists. He urged all those who received the plates for trial to complete their trials as soon as possible, so that the plates might be forwarded to the next person. In this way a great deal of time could be saved. The importance of temperature in the observations was referred to, especially in the light of the paper read by Dr. Wiley before the congress, showing the great variations in polarization in quartz plates in sugar solutions produced by variations in temperature. The importance of securing quartz plates in some way so that changes of temperature would not subject them to pressure, was fully discussed. Dr. Wiley called attention to the fact that the quartz wedges in compensating instruments were subject to the same influences, and therefore that they should be mounted in the same way as the quartz plates to avoid pressure by changes of temperature.

A general agreement was made to the proposition to substitute for all the different flasks in use a true decimal flask holding exactly 100 cc. To avoid expensive changes in polariscopes already in use, it was decided advisable to change normal weights of sugar employed in polarization to correspond to the flask. For the ordinary instruments, in which the normal weight for the Mohr flask is 26.048, the normal weight for the true flask is almost exactly twenty-six grams. For industrial purposes it was decided that it was not advisable to practice the inversion method of polarization with raw sugars. The slight errors which are introduced into polarization by the invert sugar are partly compensated for by the volume of the lead precipitate. As quickness of work is important in commercial operations, the introduction of the inversion method would be more objectionable than the slight errors which result from the single polarization. The use of animal charcoal for clarifying sugar solutions was condemned on general principles, on account of its high absorptive power for sugar.

The importance of introducing uniform methods of examination in all countries was unanimously acknowledged, but it was also stated that an attempt of this kind would be attended with serious obstacles and could only be accomplished gradually. It was voted that the chairman, with the aid of the members of the commission, prepare a comprehensive review of the analytical methods used in various countries, as well as of the regulations which are followed in checking disagreeing analyses. This compilation of methods is to be used by the committee in a final report on a uniform international method of working.

Excursions and Scientific Visits.

Numerous excursions to points of general and scientific interest were offered to the congressists.

IMPERIAL JUBILEE EXPOSITION.

Special entrance cards at a reduced rate were offered to members to visit the Imperial Jubilee Exposition located in the Prater. This exposition is held in honor of the fiftieth year of the reign of the Emperor Francis Joseph I. The buildings are situated in a pleasant part of the Prater, and are well placed and built with fine architectural effect. The exposition itself possesses the salient features of modern affairs. During the day, and especially in the evening, excellent bands and orchestras provide delightful music, which is given under cover in inclement weather. The formal visit of the congress to this exposition took place on Sunday afternoon, July 31st.

EXHIBITION OF ALCHEMIC MEDALS, ETC.

The most interesting collection of objects relating to alchemy was opened to the congressists free of charge on Wednesday, July 27th, and Saturday, July 30th. This collection is the property of the Imperial family, and was kindly lent by the Emperor especially for the entertainment of the members of the congress. That Vienna was one of the centers of alchemy, was shown by the address of Prof. Bauer.

EXCURSION TO KAHLENBERG.

On the afternoon of Friday, July 29th, the excursion to Kahlenberg took place. From this renowned overlook hill the city of Vienna may be seen in all its beauty. In the words of the late Crown Prince Rudolf, "This Imperial capital city, with its magnificent buildings, the old Stephan's Dom, index of centuries of greatness, in their center, situated on the majestic Danube, surrounded with a wreath of attractive mountains, vine-clad hills, and waving forests, so beautiful, so rich in past honors, and still so young and blooming, is a picture such as no other metropolis in the world can present."

On the plateau of the Kahlenberg Hotel a dainty luncheon was served, enlivened by a well-trained quartette of Old Vienna singers. Unfortunately a thunder storm coming on later in the evening brought to a hurried close an otherwise most delightful occasion.

VISIT TO THE WINE CELLARS IN KLOSTERNEUBERG.

By invitation of Prof. Dr. Roessler, the congressists had an opportunity to visit the celebrated Stifftkellers in Klosterneuberg on July 30th. After spending the afternoon in studying the various processes of wine manufacture and visiting the cellars, the members were entertained with " eine gessellige Zusammenkunft im Stifftshank," which was most thoroughly enjoyed.

VISIT TO THE GAS WORKS.

After the formal visit to the exposition on Sunday, those members who desired to go were driven to the city gas works in Bezirk Semmering, where the methods of supplying the city with gas were explained in detail.

VISIT TO THE SEED CONTROL STATION.

Members interested in testing the purity and vitality of seeds were given an opportunity to visit the Agricultural-botanical Experiment Station on Monday, August 1st. The director of the station, Dr. Weinzierl, conducted the visitors through the various laboratories, and explained the methods of determining the purity and vitality of seeds.

VISIT TO THE IMPERIAL OPERA HOUSE.

All delegates from foreign countries were invited to occupy stalls at the Imperial Opera House on the evening of August 2nd. The representation of " The Bride of Corea," a grand ballet with numerous tableaus descriptive of Corean life, was given with an artistic perfection which exacted the greatest enthusiasm. The Americans especially enjoyed the tableaus of the great naval fight between the Chinese and Japanese, which were given with great effect.

EXCURSION TO SEMMERING.

The official excursions connected with the congress were brought to a close on Wednesday, August 3rd, by a visit to the Austrian Vorderalpen at Semmering. The distance of the Semmering from Vienna is about seventy miles, and the trip was made through a most pleasing valley and over a gentle, but continuous, acclivity. The altitude of the hotel which overlooks the collection of mountains and valleys constituting the Semmering is 1,200 meters. A clear sky and medium temperature served to make the day more agreeable and the views more distinct. From the hotel the Schneeberg, which is the source of the Vienna water supply, is plainly seen. The melting snow, which is the source of the water supply in summer, insures to Vienna an inexhaustible supply of cold, clear, and pure water, quite in contrast with that supplied to many other European cities. After spending the day in strolling over the shady paths and sitting in the shade, and admiring the landscape in ever-changing lights, the congressists assembled at 5 P.M. on the terrace of the hotel for a final banquet. After the dinner was served, a number of farewell addresses was made. The American delegate, in thanking the organizing committee for the many courtesies which he and his colleagues had received, expressed the hope that at no distant day an opportunity might be given to American chemists to reciprocate the favors which they had enjoyed. He feared that a summer meeting of the congress in Washington would not develop a need for overcoats, but ventured to prophesy that the reception which foreigners would receive would be at least as warm as the weather. He would undertake to at least ask the Secretary of the Navy to supply a magnificent transport to convey foreign delegates across the water, where the cementation of international friendship would be made stronger. Chemistry, which had made war so destructive, was destined, in the end, to secure universal peace and good will.

Banquets and Receptions.

In addition to the excursions and visits which have already been described, a number of luncheons, banquets, and receptions were offered either to all or to certain groups of members. The most elegant and numerously attended of these was given by the Burgomaster of Vienna, Dr. Lueger, at the Rathhaus, on Friday, July 29th, from 12 to 2 P.M. At the opening session of the congress, Dr. Lueger gave the following cordial invitation to the congress to accept the official hospitality of the city of Vienna:

"Permit me, honored sirs, as mayor of the City of Vienna, to extend to you a most cordial greeting. Permit me, first of all, to thank you for having Vienna as the place of your meeting. The commonwealth of Vienna will follow your deliberations and conclusions with the greatest attentiveness. Chemistry has become necessary to every step of public life. If we want to know whether water is good or not, we must ask the chemist. If we want to know whether what is bought as human food is wholesome or not, we must ask the chemist. When we wish to know whether a given soil is fit for this or that purpose, we must ask the chemist. Therefore it is of the highest advantage to us that these gentlemen who devote their studies to applied chemistry have chosen to meet here. You will now permit me to repeat orally the already published invitation from the Common Council and Aldermen of Vienna to visit the City Hall to-morrow to break off for an hour or two from your scientific duties, in order to enjoy a lively reunion. Such interruptions of scientific efforts, as each one knows, serve to strengthen the mind in a most marked manner, and are absolutely necessary to reach happy and successful conclusions. I hope that to-morrow I shall be permitted to welcome all the chemists of the whole earth at the City Hall. It is understood that I also will greet with great pleasure the chemists of the gentler sex. Allow me to close with the wish that the results attained by you shall meet with full and complete success, and that, contended with the end of your labors, you may have a happy return to your homes. Again, in the name of the city of Vienna, I greet you."

At noon the members of the congress assembled in the reception room of the Rathhaus, and for once the "chemists of the gentler sex" attended in great numbers. An hour was spent in visiting the paintings and collections in the various halls of the building. The members and their women friends then gathered in the dining-room, where they were again cordially welcomed by Dr. Lueger, and proceeded to act on his suggestion to hold a "lively meeting." Most convincing proofs were forthcoming to show that the Burgomaster had indulged in no empty phrases in extending the city's hospitality. So lively had the meeting become that it was with great difficulty that the postprandial orators could make themselves heard. At the close of the banquet the members assembled in front of the Rathhaus, and a photograph of the party was made.

DINNER GIVEN TO THE FRENCH GROUP.

On Friday evening, July 29th, Mr. Maurice Deutsch gave a dinner in Sacher's Garden to the French members, to which your delegate had the honor of being invited. The elegant dining-room of this famous restaurant was beautifully decorated, and a dinner of the highest artistic and gastronomic perfection was served. After-dinner addresses were made by Messrs. Deutsch, Moissan, and Wiley. Sixty guests enjoyed Mr. Deutsch's cordial hospitality.

DINNER GIVEN TO THE INTERNATIONAL COMMITTEE ON THE UNIFICATION OF METHODS OF SUGAR ANALYSIS.

The Austrian Society of Beet-sugar Industry gave a dinner at the Hotel Bristol, on Monday, August 1st, to the members of the International Committee on the Unification of Methods of Sugar Analysis. Thirty guests were present. Dr. Herzfeld, the president of the committee, occupied the seat of honor at the right of Director Ströhmer, who presided at the dinner. After the coffee was brought on, Dr. Herzfeld spoke of the work already done by the committee, and of the aims it had in view. The discussion was continued at great length by other members, and the meeting adjourned at midnight with a sense of having accomplished a great deal of good work in conjunction with a most delightful social occasion.

OFFICIAL BANQUET.

The banquet given by the congress to the delegates from foreign countries was held on Sunday evening, July 31st, in the restaurant in the Volksgarten. It was at first intended to have the tables in the open garden, but the weather having become very cold compelled the removal of the tables, at the last moment, to the circular dining-hall surrounding the court of the restaurant. The presiding officer was the minister of commerce, the president of honor and the acting president sitting at his right and left. The vice-presidents and delegates from foreign countries sat to the right and left of the two presidents. The banquet was followed by after-dinner speeches by the presiding officers and delegates from foreign countries.

Chemical Laboratories in Vienna.

All the chemical laboratories of Vienna were thrown open to the congressists, but no formal visits were made thereto. The members, singly or in groups, visited the laboratories at such hours as proved to be the most convenient.

THE UNIVERSITY LABORATORIES.

There are three distinct chemical laboratories connected with the university.. The first laboratory occupies the most of the parterre of the Chemical Institute, No. 10 Währingerstrasse. It contains working desks for seventy students and for twenty-one advanced students and assistants. The professors and assistant professors occupy six smaller halls. There are two balance rooms, but only thirteen balances for all the students. The number of students received is limited to the desks available, and consists of those students of the university who are candidates for degrees in pharmacy or philosophy. The number of papers, theses, etc., which have been published from the laboratory is 285. The director of the laboratory from its foundation to 1876 was Hofrath Prof. Dr. Franz Karl von Schneider, from 1876 to 1890 Hofrath Prof. Dr. Ludwig Barth von Barthenau, and the present director is Prof. Dr. Hugo Weidel.

The second university laboratory occupies the whole of the first story of the Chemical Institute, and contains two large working rooms for beginners and seventy desks for advanced students. There is also a large number of small laboratories for the use of the professors and assistants. As is the case with the first laboratory, it contains a small library, where the leading chemical journals and works of reference may be found. From this laboratory, since 1876, 292 original papers have been published. The present director is Hofrath Prof. Dr. Adolf Lieben.

The third laboratory connected with the university is situated at No. 1 University Place. It is devoted especially to analytical chemistry, and four preparative rooms for the experimental lectures. The director of this laboratory is Prof. Dr. Eduard von Lippmann.

The laboratory for medical chemistry is also a part of the university system under the Pathological Institute and is devoted especially to practical medical studies. It is situated in the general hospital building in Spitalgasse. It is provided with 48 working desks, and 10 for advanced students. In addition to these are found the laboratories for the professors and assistants. The number of the students is limited, and consists exclusively of those who are candidated for the degree of doctor of medicine. The papers of the laboratory are published partly in medical and partly in chemical journals. The director of the laboratory is Hofrath Prof. Dr. Ernst Ludwig.

LABORATORIES OF THE TECHNICAL HIGH SCHOOL.

The Austrian Technical High School corresponds to our Institute of Technology, and the one at Vienna is justly celebrated. There are five laboratories connected with this school.

1. The laboratory for general chemistry consists of six rooms in the parterre of the school building. The teachers and advanced students of this laboratory are occupied with researches of a scientific and technical nature. The director of this laboratory is Hofrath Prof. Dr. A. Bauer.

2. The first laboratory for chemical technology of organic bodies is located on the court of the school building, and consists of two separate halls. The first has desks for twenty students, balance rooms, preparation rooms, etc. The second has the same number of students' desks, but is used for the advanced students and for research. The director of this laboratory is Prof. Dr. Hugo Ritter von Perger.

3. The second laboratory for chemical technology of organic materials is one of the largest belonging to the high school. It occupies thirteen rooms in the middle area of the building. Students of the third year's course are received in this laboratory, and also officers of the technical troops (engineers, sappers,

and miners). The students are occupied chiefly with studies in organic chemistry. The director of this laboratory is Prof. Johann Oser.

4. The laboratory for analytical chemistry embraces eleven rooms on the first story of the school building, and has desks for 118 students. The director of this laboratory is Prof. Dr. G. Vortmann.

5. The laboratory for fermentation and bacteriology is the latest addition to the chemical equipment of the high school. It was founded in 1897, and during its first year enrolled twenty-seven students, of whom two were foreigners. It is equipped with all the latest apparatus for studying the phenomena of fermentation and bacterial activity. The director of this laboratory is Dr. Lafar.

LABORATORIES OF THE IMPERIAL HIGH SCHOOL FOR AGRICULTURE.

There are two laboratories connected with this institute:

1. The laboratory for field and forest chemical technology was opened in 1872. It consists of a chemical and fermentation-physiological department, the latter having just been established. The chemical laboratory embraces two large halls, each arranged for sixteen students. In addition, there are balance rooms, photographic ateliers, and separate laboratory rooms for the professors and assistants. There are also a large lecture-room and a special room for microscopic research, storerooms, etc. Only students of the School of Agriculture are received in this laboratory who have had at least three semesters in the laboratory for general chemistry. The program of studies embraces researches in the chemistry of sugar, starch, malt, beer, and alcohol manufactures, as well as in wine-making. The course lasts for two semesters. The director is Hofrath Prof. Dr. Schwackhöfer.

2. The laboratory for general and agricultural chemistry embraces a suite of fourteen rooms, desks for ninety-eight students, laboratories for professors and assistants, and all modern appliances for chemical agricultural studies. The director is Prof. Dr. G. Zeissel.

CHEMICAL LABORATORY OF THE GEOLOGICAL SURVEY.

This is one of the oldest laboratories in Vienna, having been established in 1849, "for the purpose of studying all kinds of soils and rocks, ores and fossils; also the different products of the mines of the Empire." A long series of publications on the chemical composition of rocks and minerals, mineral waters, and on crystals and crystal formations, has issued from this laboratory and been published chiefly in "Verhandlungen der k.k. geolog. Reichsanstalt," or in the "Jahrbuch der k.k. geolog. Reichsanstalt."

The laboratory was at first under the direction of Dr. F. Ragskys, and after him came Dr. Karl von Hauer. At first the chemists in this laboratory had no official standing, and only in 1872 were they recognized as of equal rank with the geologists. Baron Heinrich v. Foull, the late director of the institute, was slain by the natives of the Solomon Islands during a visit there in 1896. The present director is Dr. Konrad v. John, who has numerous assistants, most of them volunteers.

CHEMICAL LABORATORY OF THE TECHNICAL MILITARY COMMITTEE.

In this laboratory the government investigations of explosives are conducted. Also all the materials, such as clothing and food, which are furnished to the army and navy, are examined in this laboratory.

CHEMICAL LABORATORY OF THE MILITARY SANITARY COMMITTEE.

This laboratory was founded in 1854, and has, for its chief purpose, the examination of drugs and medicines, and medicinal supplies furnished to the army and navy. The director is Dr. Florian Kratschquer.

IMPERIAL GENERAL RESEARCH INSTITUTE FOR FOODS.

This is one of the latest foundations of the governmental scientific institutions, having been opened on the 1st of December, 1897. It is charged with the official inspection of the trade in all kinds of foods and drinks consumed by man. In addition to its official duties, this institute is authorized to make examinations of foods and drinks for private persons on the payment of fixed fees. This work, however, may be refused if it conflict with official duties. The chemists employed here must have diplomas showing that they are food experts. The scientific staff of the institute is also charged by law to make researches in respect of the composition and properties of human foods and the best methods of studying them. The director of the institute is Dr. Max Grueber, professor of hygiene in the Vienna University.

CHEMICAL LABORATORY OF THE GENERAL POLYCLINIC.

The studies of this laboratory are directed mainly to pathological products, serums and other products of biological activity, with special reference to diagnosis and therapeutics. It has roomy and well-illuminated quarters, and is under the direction of Dr. Julius Moultner, university professor of applied medical chemistry.

THE IMPERIAL AGRICULTURAL CHEMICAL EXPERIMENT STATION.

This institution is the head of all the agricultural experiment stations of the Austro-Hungarian monarchy. It was established in 1870, and now is located in commodious quarters at No. 3, Trunnerstrasse, in the Second Bezirk. The first director of the station was Dr. Ignatius Ritter von Moser. From his death until the spring of 1898 the station was under the direction of Prof. Dr. Meissl. In the spring of that year Dr. Meissl was made emeritus professor and transferred as advisor and technical assistant to the ministry of agriculture. Prof. Dr. Dafert has just been called to the directorship of the station, with Prof. Joh. F. Wolfbauer as his first assistant. This laboratory is charged with the general direction of all the great problems underlying agricultural progress; *viz.*, researches in animal and plant production, acclimatization of plants and animals, fertilizer control and analysis, making chemical, microscopical, and physiological investigations for the minister of agriculture, and, under certain conditions, for private citizens. The station is also charged with giving advice and instruction on agricultural subjects, and with training of agricultural experts. In general, this station holds the same relation to the minister of agriculture that the Divisions of Botany, Vegetable Pathology, Soils, Biochemistry, and Chemistry hold to the secretary of agriculture, in Washington. In connection with the station a vegetation house has been established at Kornenburg for practical demonstrations in plant nutrition and physiology, similar in every respect to the vegetation house of the Division of Chemistry, at Washington. The feeding experiments are conducted in a large respiration apparatus, built, in general, according to the Pettenkofer plan. Extensive experiments of a chemical-physiological nature are made with calves, cows, sheep, pigs, and even horses. This institute claims the credit of being the first to demonstrate beyond question that the carbohydrates are the chief source of all the fat of the animal organism. Among some of the subjects more recently investigated in this laboratory may be mentioned the composition and value of the different foods of the Austro-Hungarian monarchy, the proteid and fatty bodies in beans of soja hispida; the cause of the superior nutritive properties of Alpine hay; the composition of the flesh of whole animals fed under different systems of nutrition; the critical examination of the methods of analysis of the different organs of the body and their secretions; the influence of fertilization; the composition of field and garden plants; and the chemical and physical properties of peaty soils. Important dairy researches have also recently been made, especially in respect of the preparation and preservation of strong extracts of rennet on the condensation and preservation of milk, and on the testing of milk and milk products for purity and adulterations. Extensive studies have also been undertaken on the properties and methods of estimation of the most important sugars as related to the theory and practice of fermentation. In connection with this study valuable contributions on the subject of the relative fermenting power of yeasts have been conducted. A study of the composition of the water of the Danube at Vienna for every day in the year has also lately been made.

In addition to this public work the institute is also authorized to undertake private analyses at a fixed price, the fees so obtained becoming a part of the available funds of the laboratory. The number of these analyses, which in 1877 reached scarcely 1,000, amounted in 1896 to 14,940. To your delegate this laboratory was naturally the most interesting of all those visited, and he is indebted to Director Dafert for many courtesies attending his visit. This chemical experiment station shows, in a most convincing manner, the fundamental position occupied by chemistry in almost every problem connected with agricultural research. In Europe, more than in America, is this relation recognized, and there is scarcely a single station of the 100 existing in Europe which does not have a chemist for a director. In fact it is doubtful whether any agricultural station in which the chemical idea is not dominant can ever reach the full measure of its usefulness, or study intelligently and successfully any of the really great problems connected with agricultural research. Of how little relative value the non-chemical researches are which are connected with agriculture may be readily seen by consulting the personnel of the European stations. This fact is mentioned with no purpose of discrediting the work of entomologists, botanists, and other scientists in relation to agricultural development, but only to recall to the thinking public the very foundation of agricultural science, which relates first of all to the productivity of the soil. The fertility of the fields is the first great need of agriculture. After that come the development of domestic animals, the study of their diseases, and the study of the adaptability of plants and the habits of useful and injurious insects.

PHOTOCHEMIC LABORATORY.

The chemistry of printing with light is studied in a laboratory connected with the Imperial Graphic Teaching and Experiment Station founded in the year 1888. This laboratory consists, first, of a section for teaching the theory of photography and graphic reproduction; second, of a section for teaching the theory and practice of illustrating books and periodicals; third, an experiment station for photochemistry and photo-printing;

fourth, a museum containing collections illustrating all the subjects of study and apparatus for producing them. The director of the institute is Regierungsrath Prof. Dr. Josef Maria Eder, professor in the Technical High School. The staff consists of five professors, four special teachers, two assistant teachers, one privat docent, and numerous helpers.

CHEMICAL LABORATORY OF THE ART SCHOOL OF THE IMPERIAL MUSEUM FOR ART AND INDUSTRY.

The laboratory was established in 1877 for the study of glass, porcelain, and enamels. In 1888 it was transferred to the ministry of religion and education, and enlarged to embrace all subjects of artistic manufacture. Instruction and practice are given on the materials, means, and methods of artistic work. The chief subjects of study, however, remain those for the investigation of which the institution was originally founded. The director of the laboratory is Prof. Dr. Friedrich Linke.

TECHNICAL-CHEMICAL LABORATORY FOR THE LEATHER INDUSTRY.

The object of this laboratory is the promotion of the leather industry by scientific researches. The technical part of the work has for its object the conversion, into practical use, of the purely scientific studies. The laboratory was opened in 1874 by the minister of commerce. It contains a physical, a chemical, and a bacteriological laboratory, and a large special library of all principal works relating to leather, its preparation and uses. In 1882 the institute was transferred to the ministry of education. Since then a special course in instruction in the theory and practice of leather production has been organized for advanced students and technical workers. The director of the institute is Regierungsrath Prof. Dr. Wilhelm Eitner.

CHEMICAL-TECHNICAL EXPERIMENT STATION OF THE CENTRAL SOCIETY FOR SUGAR INDUSTRY.

Next to the agricultural chemical experiment station, this laboratory had the greatest interest for your delegate, and it was the only one to which he had time to make a second visit. It is under the direction of Prof. Dr. Friedrich Strohmer, the genial general secretary of the congress, assisted most ably by Dr. Anton Stift, one of the recording secretaries. Unfortunately for the chemical visitors, the laboratory was somewhat torn out preparatory to moving to the more commodious quarters which it will soon occupy at No. 18 Elizabethstrasse, Bezirk 1. The laboratory was founded, in 1859, by the Union for Beet-sugar Industry of the Austrian Empire. In 1867 the laboratory was transferred to Prag, at that time the center of the beet industry in Austria. In 1869 it was moved to Gross-Seelowitz, the seat of some of the most important sugar factories of the Empire. One year thereafter the station was removed to Vienna, where it has remained ever since, and where it is now permanently located. The station is entirely independent of governmental control or assistance, and is the property of the Central-Verein für Rübenzucker-Industrie. Its purpose is the investigation of all subjects connected with beet-sugar production, whether of an agricultural, chemical, or technical character. The station also edits the journal of the society, the *Wochenschrift des Central-Vereins für Rübenzucker-Industrie* in den Oesterr.-Ungar. Monarchie. Private analyses for sugar growers and others are also made by the station at a fixed tariff, the fees derived therefrom becoming a part of the funds to sustain the station. From 1870 to 1898 there were made at the station 99,036 analyses, involving 223,120 quantitative determinations. The laboratory undertakes also to set standard solutions for the use of technical chemists in the various sugar factories, to adjust polariscopes and graduate flasks. Special botanists, entomologists, and pathologists are also employed for the study of beets, beet diseases, and injurious insects and molds. In the new quarters, to which the laboratory is about to be moved, greatly increased facilities for work will be provided, and under the able direction of Dr. Strohmer the station may be expected to accomplish even greater works than in the past.

CHEMICAL LABORATORY OF THE GENERAL AUSTRIAN DRUGGISTS' UNION.

This laboratory was founded in 1865, and has, for its chief object, teaching the theory and practice of pharmacy. A specialty is made of urine analysis for diagnostic and therapeutic purposes. The director of the laboratory is Dr. C. Glücksmann.

RESEARCH-INSTITUTE OF THE GENERAL AUSTRIAN DRUGGISTS' UNION FOR FOODS, CONDIMENTS, AND DRINKS.

This laboratory was founded in 1888 in honor of the fortieth year of the reign of the Emperor. Its chief purpose is the analysis of all kinds of foods, condiments, and drinks for associations and private individuals, at a charge varying in amount with the magnitude of the work. It also gives instruction to graduates in pharmacy who wish to prepare themselves especially for food and drug analysis. A special course of lectures is given on food adulteration. The director of the laboratory is Dr. Moriz Mansfeld.

AUSTRIAN EXPERIMENT STATION AND ACADEMY FOR THE BREWING INDUSTRY.

This institute possesses one of the best appointed and most complete laboratories for its purpose of any in Vienna. It was founded in 1887, but the Academy of Instruction was first opened in 1895. The laboratories of chemistry, fermentation, bacteriology, and botany are not only roomy and admirably equipped, but united in an organic union highly conducive to the best results. Each worker is not engaged alone in pushing his own researches, neglecting and even despising the work of others, but all in perfect harmony and under a single direction, are working together for one great purpose; namely, the placing of the brewing industry on a strictly scientific basis and promoting its progress by research and experiment. The course of instruction lasts for four semesters, and an entrance examination equivalent to that required for the voluntary one year military service is exacted. Foreigners also, who desire to pursue the course of study, must bring evidence of a suitable education. An experimental malt factory and brewery are connected with the station, where the results of all researches are subjected to practical demonstration. The director of the institute is k. k. Hofrath Fr. Schwackhöfer. The chief of the chemical laboratory is Dr. Ed. Jalowetz, and of the ferment-physiological laboratory, Dr. H. Wichmann.

CHEMICAL LABORATORY OF THE K. K. TECHNOLOGICAL TEXTILE MUSEUMS.

The object of this laboratory is to give theoretical and practical instruction to students proposing to enter the textile fabrics industry. It is one of the largest institutions of instruction in the world, and the annual expenditures of the institute amount to about 265,000 gulden. Since its foundation in 1881 more than 10,000 students have taken the course of instruction. The laboratory and school of instruction are under the direction of Dr. Paul Friedlander, who is assisted by a large corps of professors and specialists. The chemistry of dyeing is, of course, the chief subject taught.

CHEMICAL-PHYSIOLOGICAL EXPERIMENT STATION FOR WINE AND FRUIT CULTURE AT KLOSTERNEUBERG.

The instructive and agreeable excursion to this locality has already been referred to. Towards the end of 1870 this important station was founded by the k. k. minister of agriculture, and Prof. Dr. L. Roessler, at that time professor in the Technical High School at Karlsruhe, was appointed director. The charter of the institute required the most thorough scientific research into all the problems connected with wine-making and fruit culture. The work in general is directed

(*a*) To a chemical, microscopical, and bacteriological study of must and wine, of yeasts and the by-products of fermentation, to studies of cellar fermentation and ripening, clarification, sucration, etc.

(*b*) To the chemical and mechanical analysis of vineyard soils.

(*c*) To the chemical studies of vineyard fertilizers and their effects upon the vintage.

(*d*) To the chemical and microscopical studies of the vine and fruit trees, with special reference to their constitution and ability to resist the ravages of diseases and insect pests.

The institution was also charged on its foundation with the publication of the results of its labors, and with furnishing advice and direction to those engaged in wine and fruit culture. The director of the station is Prof. Dr. Josef Leonhard Roessler, who showed many courtesies to the members of the congress who visited the station, both on the occasion of the general excursion and at other times.

The above brief review of the foundations for teaching chemistry and chemical practice in Vienna has been given as a proper adjunct to the special report of the congress, and because American chemists are not, as a rule, so well acquainted with the facilities for teaching chemistry in Vienna as they are with those in Germany and France. It is seen that there is no dearth of laboratories and experimental stations in the Austro-Hungarian capital, and the rulers of that eastern Empire are fully alive to the fact that only those nations which push chemical studies and apply them in a scientific technical manner can hope to keep abreast of the progress of the world.

These Congresses of Applied Chemistry teach, first of all, the fundamental relations of applied chemical research to all the great industries that make nations wise, rich, and powerful. The advance of any nation in wealth, civilization, and power is measured directly by the position occupied therein by chemical research applied to the arts and sciences.

And yet the makers of the wealth of nations, those who contribute most to its progress and welfare, who are most intimately related to all the industries of war and peace, strange to say, receive the least social and political distinction, and command the least compensation of all the classes who devote themselves to the public service and welfare. It is therefore suggested that a proper theme to receive the attention of the next congress, which meets in Paris in 1900, would be a " Report on the Fundamental Relations of Applied Chemistry to National Wealth and Progress."

H. W. WILEY.

NOTE.

A Convenient Method for Maintaining Reduction of Ferrous Solutions[1].—My reasons for calling attention to this method for maintaining reduction in ferrous solutions are, that it is economical, convenient, and effective, and so far as I have been able to ascertain, new, in this particular application.

Various methods have been used to keep ferrous solutions reduced, such as the introduction of zinc and sulphuric acid, and the addition of sirups, gums, sulphurous acid, or sulphuric acid. These are either unnecessarily expensive, or ineffective, as they may interfere with the uses of pure ferrous solutions, and I have not been able to obtain as satisfactory and permanent results with them, as with the method which I have made the subject of this note; namely, the addition of ten per cent. of concentrated sulphuric acid and a suitable amount of iron in the form of small wrought iron nails, to a ten per cent. solution of ferrous sulphate. The acid under these conditions liberates hydrogen very slowly, and yet fast enough to nullify the oxidizing action of the air, even when the solution is exposed in an open beaker.

I have found that ferrous solutions thus made up will keep for more than a month in a practically unchanged condition, while solutions made up with sirups, gums, or with free acids and similarly exposed, were very largely ferric at the end of the period, and acidified ferrous ammonium sulphate, $FeSO_4(NH_4)_2SO_4+6H_2O$, was in very little better condition.

When one requires a large amount of ferrous sulphate for qualitative classroom work, for example, an open beaker full of the reagent always in good condition, is very useful in saving time, and is of great convenience, and in these respects has been so satisfactory to me, that I venture to present the method to the members of the society.
WILLIAM S. MYERS.

Rutgers College, June 3, 1898.

NEW BOOKS.

ELEMENTS OF GENERAL CHEMISTRY WITH EXPERIMENTS. By JOHN H. LONG, M.S., Sc.D. Chicago: E. H. Colegrove. 1898. Price, $2.00.

This is a compact text-book, filling only 408 pages, underta-

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[1] Read before the New York Section, June 3, 1898.

king to give an introduction to the main principles of chemical science, an outline of the descriptive chemistry of the elements and their leading inorganic combinations, accompanied with directions for simple experiments by the student. In its preparation the author has used a part of his work "Experimental and Analytical Chemistry," now out of print, and has added new subject-matter, making it all anew as a text-book of elementary general chemistry, preparatory to the work of analysis.

Only the phenomena of physical and chemical change are presented in the introductory chapter; volume proportions are brought forward in the chapters upon oxygen, hydrogen, and chlorine, and it is not until following chapters that the atomic theory is broached, which is done with an excellent summary of its historical development. Still later on the subject of valence is presented, and some uses of structural formulas are set forth. Throughout the book the uses of equations and of constitutional formulas are quite carefully guarded against abuse, but as aids to study they are not by any means neglected.

In respect to solubilities the facts of saturation, precipitation, and crystallization are clearly distinguished in the very beginning of the book, but electrochemical theories of solution are not introduced at all.

The periodic system is brought forward when the metallic elements are taken up, together with further treatment of the subject of valence and of the determination of atomic weights. After this the periodic arrangement of the elements, well termed the *natural* arrangement, is observed through the remainder of the book.

In all the chemical descriptions, illustration is drawn from the relations of organic life and from the manufacturing arts, with justice to the present state of industrial chemistry.

The directions for experiments, distributed through the work, extend to 173 numbers. The author states that these experiments represent the work required in his classes during the past ten years' work, as it would appear, "repeated by the student in the laboratory" after like demonstration by the teacher in the classroom. Such exercises, following those of the lecture-table, undoubtedly serve, as the author says, to fix, as by repetition, the subject-matter of the lectures in the memory and mind of the learner, with great advantage. But it may be doubted whether initiative exercises of this order will serve to develop the independent power of the student as well as a series of laboratory exercises planned expressly for the student, distinct from the order of the lecture course though on the same subject.

It remains to mention what is best about this book; namely, its personality, clearly recognized in every page by those who know the author and by those who have read his contributions. Personal qualities can be known more easily than named, but it can be said that the authorship of this little book is characterized by simplicity in description, directness in statement, breadth of view in science, caution in adoption of theory, care against misinterpretation, and experience with the applications of chemistry at the present time. A. B. PRESCOTT.

INTRODUCTION TO CHEMICAL-TECHNICAL ANALYSIS. BY PROF. F. ULZER AND DR. A. FRAENKEL, Directors of the Testing Laboratory of the Royal Technological Museum in Vienna. Authorized translation, with an appendix by the translator, HERMAN FLECK, Nat. Sc.D., Instructor in Chemistry, University of Pennsylvania. Philadelphia: P. Blakiston's Son & Co. vii + 188 pp. Price, $1.25.

This book is apparently an effort to teach the student "something of everything" while the "everything of something" is left to the special treatise. Unfortunately the methods described under the different branches of technical work are generally very sketchy and few of them are capable of execution by the student without assistance.

The subjects treated include Products of Technical Chemistry, Cement and Clay, Metallurgical Industry, Alloys, Fertilizers, Sugar Industry, Fermentation Industries, Fats, Waxes and Mineral Oils, Mordants and Tanning Materials, Textile and Dyeing Industries, Products of the Coal-tar Industry, and in an appendix, White Lead, Manganese Dioxide, Bleaching Lime, etc., Asphalt and Food Stuffs.

The subjects most satisfactorily treated are the "Mordants and Tanning Materials" and the "Textile and Dyeing Industries." The one most unsatisfactorily treated is the "Metallurgical Industry."

The appearance and printing of the book is good and the index is well made, but the cross references in the body of the book are far from satisfactory. For instance, on page 99, Kjeldahl's method is referred to as under "Nitrogen Fertilizers," page 78, whereas it is really under the head of "Nitrogen," page 74. On page 154 the chemical analysis of starch is referred to as being in Chapter VI, whereas it is really in Chapter VII, page 99.

Some proper names are misspelled, as Candlon for Candlot, page 39, and Brown for Drown, page 51.

ANDREW A. BLAIR.

COMMERCIAL ORGANIC ANALYSIS. BY ALFRED H. ALLEN, F.I.C., F.C.S. Second edition. Vol. IV. Philadelphia: P. Blakiston's Son & Co. 1898. 8vo. 584 pp. Price, $4.50.

This work needs no introduction. The three earlier volumes—or rather five, for the third volume is really three in one—have gained a most enviable reputation, and have rendered more assistance than any other publication to those who have to do with proximate organic analysis. We have awaited this final volume of the work, therefore, with interest, and welcome its appearance most heartily.

The work is thoroughly up to date, including the most recent contributions to the literature of the field it covers. The author has evidently intended to give references to articles mentioned, and has usually done so, but unfortunately the reader is often referred to abstracts instead of original articles.

As stated in the preface, " Much of the matter of Volume IV is scarcely such as might be expected to be contained in a work purporting to treat of commercial analysis." This could not well be otherwise, for some of the subjects treated are among the most difficult to study and the least understood of all commercial products.

The subject-matter of the volume is arranged under the headings, " Proteids and Albuminous Principles," and " Proteïds of Albuminoïds." The first 460 pages are of equal interest to the physiological chemist and the food chemist. Here are treated the proteids of eggs, blood, urine, and milk, as well as vegetable proteids, and methods are given for the examination of dairy products and of meat and meat products. The proteids of digestion, and methods for the examination of blood are also discussed at length.

The sixty-eight pages devoted to meat and meat products are especially worthy of note, though the apparatus described for the estimation of nitrogen (p. 32) would scarcely meet with the approval of our agricultural chemists.

The remainder of the volume is devoted to the proteoïds. The author has set for himself the very difficult task of classifying the bodies that come under this heading, and this treatment of them is probably as systematic as is possible with the knowledge we now possess of their properties.

The nomenclature of this subject is most bewildering, at present, so much so that it is necessary for a writer, in order to be understood, to give his interpretation of even the terms most commonly employed. Some writers, and even national associations, in trying to assist us, only add to our perplexity. We are glad to see, therefore, that the author of this work has striven, first of all, to promote uniformity, for instance, the term "albuminoïd" is used with the same significance as proteoïd, but it is suggested that, to prevent confusion, it be avoided whenever possible.

On the whole the volume compares favorably with the earlier volumes of the work, and cannot but do much to remove the difficulties that are encountered in the examination of nitrogenous compounds.

W. D. BIGELOW.

MANUAL OF DETERMINATIVE MINERALOGY, WITH AN INTRODUCTION ON BLOWPIPE ANALYSIS. By GEORGE J. BRUSH. Revised by SAMUEL L. PENFIELD. Fifteenth edition. pp. 302. New York: John Wiley & Sons. 1898. Price, $4.00.

This book is so well known through its fourteen previous editions that it is surely superfluous for the reviewer to do anything more than to note the additions and changes which have been made, and to call attention to what appear to be defects or deficiencies.

The additions consist principally of a well-written and useful chapter on the physical properties of minerals, the greater part of which deals with crystallography, and, further, in the introduction into the tables of such well-defined mineral species as have been discovered in the twenty years since their last revision.

The most evident change has been in the reconstruction of the tables, with the dominant idea of making the chemical tests the more decisive ones and physical tests principally subordinate. In doing this, the author has our most sincere approval; we felicitate him on the extent to which he has emphasized this change. When reviewing Dr. Frazer's tables for the determination of minerals by physical properties,[1] we felt constrained to remark that "every true scheme of determining minerals should start with and be based on their chemical composition, bringing in physical tests afterwards, etc.," and on this ground we condemned methods based on physical properties as "starting at the wrong end, and unfit to guide in the accurate determination of minerals in general." We therefore believe that Prof. Penfield has increased the accuracy and utility of his tables in proportion as he has brought the chemical tests forward as the primary ones and relegated the physical tests to their logical subordinate position. That he is thoroughly convinced of the desirableness of this tendency may be seen from the following extracts:

"It is believed that no methods are so generally to be relied upon for giving decisive results as those based upon the identification of the chemical constituents of the minerals."

"The tables have been so developed that tests for characteristic chemical constituents furnish the chief means for identification."

Our chief criticism of the method of the tables is that the author has not made these changes radical enough, that he still holds on to some physical tests as primary; whereas, to be consistent, he should have relegated them all to their proper subordinate position. The retention of luster and fusibility as primary divisions is the last relic of the former illogical and unsatisfactory method of classification, and it is to be regretted that the author did not perceive the desirability of retiring these from their too prominent function and thus coming at once to the logical simplicity of the chemical basis as primary.

It is in our judgment a defect of the book that many quick, decisive, and reliable blowpipe tests are not accounted at their proper value, and the recommendation usually given to make the corresponding wet test in their place. We think that the author undervalues the reliability of many flame and bead tests

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[1] This Journal, 17. 353.

especially, which when carefully performed are really more decisive and satisfactory than the wet tests, besides being more quickly made and with simpler apparatus and reagents.

Another general defect is that the tables still fail to take account of some of the most common and practically inseparable impurities occurring in minerals. We cheerfully allow the truth of Prof. Penfield's remark that "it would be impossible to devise blowpipe methods to meet the contingencies arising from the various mixtures of minerals"—but does that excuse the classifier from taking into consideration the most frequently occurring isomorphous replacements which introduce foreign elements into the mineral?

To particularize: On page 246 are given the fusible minerals with metallic luster containing arsenic. The second mineral mentioned is characterized as containing both arsenic and antimony, leaving it to be implied that the thirty minerals following are free from antimony, and it is true that no antimony appears in their formulas. But it is nevertheless the fact that eleven of these thirty do often contain antimony, in amounts varying from four and eight-tenths to twenty-eight per cent., and that therefore any one of these eleven might, at times, give the reaction ascribed only to allemontite. Once again, on page 249, are given antimony compounds with lead, combined with first copper, then bismuth, silver, tin, and finally without any of these four elements. Yet, among the ten minerals in the last class, the simple fact is that six of them do at times contain enough copper (one to six per cent.) to give the reaction which would place them with bournonite, in the first class. These are only two instances of what could be illustrated in almost every division of the classification.

The question at once arises—Is an omission to take such cases into the account unavoidable? Would it be an impossible task to catalogue each mineral in every class into which its occasionally occurring inseparable impurities would unavoidably cause it to fall in practice? If that is in reality impossible, then we owe an apology to the author for dwelling on an unavoidable defect; for a defect it certainly is, since a mineral will, in general, fall into its correct place in the table only when it is the typically pure substance which the formula represents.

The adoption of the chemical basis of classification inevitably requires that variations of the composition of a mineral from the normal must be taken into account, when they affect its position in the classification. When such a classification, on the chemical basis, is *perfectly* carried out, then we will possess a theoretically perfect system of determinative mineralogy.

To sum up, then, this book is, in our judgment, the best treatise on determinative mineralogy that is yet published; but the tables have some defects of method and many deficiencies of detail, the correction of which would greatly increase their reliability.

JOSEPH W. RICHARDS.

A TEXT-BOOK OF VOLUMETRIC ANALYSIS WITH SPECIAL REFERENCE TO THE VOLUMETRIC PROCESSES OF THE PHARMACOPOEIA OF THE UNITED STATES. BY HENRY W. SCHIMPF, PH.G., M.D., Professor of Inorganic Chemistry in the Brooklyn College of Pharmacy. Third edition, revised and enlarged. New York: John Wiley & Sons. 1898. xxx + 522 pp. Price, $2.50.

In its present form this work consists of four parts: Part I gives a description of the apparatus, indicators, methods of work and of calculation used in volumetric analysis, and also a concise statement of the methods to be used for the inorganic substances of the U. S. Pharmacopoeia. Part II is new and gives methods for the analysis of various medicinal acids and metallic salts. Part III is devoted to sanitary analysis and includes especially methods for the analysis of water, milk, butter, starch in cereals, diastasic value of malt, glycerin, alkaloids, vegetable drugs, and surgical dressings. Part IV gives gasometric methods for the analysis of carbonates, nitrous ether, nitrates, urea, and hydrogen dioxide.

The descriptions and directions are mostly clear and satisfactory, and the methods given are usually well suited for the purposes for which they are designed. Two or three matters of detail may be criticized: magnesium chloride is now generally used for magnesia mixture instead of magnesium sulphate, as recommended (p. 241). The standards for nitrites in potable waters (p. 313) do not agree with the opinion of the best authorities and should be revised. A table of atomic weights based on O = 15.96 is decidedly out of date, but that may be the fault of the pharmacopoeia rather than of the author.

Perhaps the most serious omission in the book is the failure to give any rational discussion of the theory of indicators in acidimetry. Since Ostwald's discussion of the subject has become so easily accessible, any book on volumetric analysis which does not, at least, give an outline of the principles involved, must be considered as incomplete. W. A. NOYES.

COMMERCIAL ORGANIC ANALYSIS. VOL. I. BY ALFRED H. ALLEN, F.I.C., F.C.S. With revisions and addenda by the author and HENRY LEFFMANN, M.A., M.D. Third edition. Philadelphia: P. Blakiston's Son & Co. 8 vo. 557 pp. Price $4.50.

This new and thoroughly revised edition of Vol. I of Mr. Allen's valuable work will be heartily welcomed by chemists everywhere. The second edition was published in 1885, and the present volume had become a necessity in order that it might rank in completeness with the later volumes of the work.

The subject-matter has been brought well up to date by material furnished by both Mr. Allen and Dr. Leffmann. Numerous typographical errors in the second edition have been corrected and the index has been much improved by very considerable enlargement. The arrangement of the subject-matter remains essentially the same as in the second edition which was eminently satisfactory. The methods of the American Association of Official Agricultural Chemists have been included, very properly, in the text.

The following subjects have had much valuable matter added to them; *viz.*, Specific Gravity, Kjeldahl Process, Proteids of Wheat Flour, Vinegar, Brewing Sugars, Malt Substitutes, Hop Substitutes, Secondary Constituents in Spirits, Formaldehyde, Methyl Alcohol, Acetone, Fusel Oil, Argol, Starch, Glucose, Invert Sugar, Lactose, and Wine. The addenda treat of "Detection of Gallisin in Beer," "Invert Sugar," "Outline Process for the Detection of Bitter Principles in Beer," "Method for Estimating Galactan," and the "Determination of Pentosans by Means of Phloroglucol." WM. L. DUDLEY.

LEHRBUCH DER ANORGANISCHEN CHEMIE. VON PROF. DR. H. ERDMANN in Halle. Mit 276 abbildungen und vier farbigen Tafeln. Braunschweig: Friedrich Viewig und Sohn. 1898. xxvi + 756 pp. Price, *M.* 18.

The author states in his preface that he has taken as his model in the making up of this volume the well-known "Lehrbuch der Chemie" of Gorup-Besanez, and that he would have called it the eighth edition of that work were it not that the changed condition of the science since its publication has rendered necessary a fundamental rearrangement of the subject-matter. The arrangement adopted is that usually followed in works of this character; *viz.*, (1) eighty-one pages of an "Introduction to Chemistry;" (2) "The Non-metals (Metalloide)" of 420 pages; and (3) "The Metals," 217 pages.

Under the first division, after a very brief explanation of the Roman and Arabic systems of numbers, and of logarithms, two pages each of a four-place table of logarithms and antilogarithms are given. Then follows a discussion of the fundamental principles of the science, such as "The Three States of Matter," "The Kinetic Theory of Gases," the "Nature of Chemical Changes," the "Atomic and Molecular Theory of the Composition of Matter," "Practical Methods of Determining Molecular Weights," the laws of "Combination of Gases by Volume," etc. The discussion of these principles is well done, and is more extended than is usually found in treatises the size of this.

The author says (p. 82): "By far the greater number of the chemical elements are solid, more or less easily fusible bodies of high luster, exceedingly opaque, good conductors of heat and electricity," etc. "These elements we call metals." As the chemist in classifying the elements for his purposes places no emphasis upon these purely physical properties, it would seem better were they classed as metals or non-metals in accordance with their base-forming or non-base-forming characteristics.

In the descriptive part of the book, the name of each element is followed by its molecular formula, its synonyms, and a list of its prominent physical and chemical properties. Then follows the occurrence of the element, its method of production, properties, and the properties of its inorganic compounds, and well illustrated directions for performing the most important laboratory experiments. Thirteen pages of text are devoted to helium and argon with illustrations of the apparatus for isolating them and examining their spectra, while a supplementary note on page 756 announces the discovery of crypton and neon. The structural formulas of many compounds are given, and molecular proportions are invariably expressed in chemical equations.

The "periodic law" is discussed in less than four pages near the end of the volume, and no mention is made in the descriptive part of the book of its aid in a rational system of classifying the elements. This neglect will appear to many chemists as a mistake of the author greatly to be regretted. Electrochemistry, the theory of solution, and ionization are also very briefly treated. The volume closes with a table of various distances, wave-lengths, etc.

The illustrations are numerous and excellent, and many of them are new to text-books of chemistry. The four lithographic charts of colored spectra are much superior to those usually published.

The work, taking it all in all, is an excellent one, and will be heartily welcomed by all who are interested in a wider diffusion of a knowledge of chemical science. W. W. DANIELLS.

PRELIMINARY REPORT OF AN INVESTIGATION OF RIVERS AND DEEP GROUND WATERS OF OHIO AS SOURCES OF PUBLIC WATER SUPPLIES. By the State Board of Health. 1897–1898.

Early in the report we find the very apt remark, that the examination of one or two samples of water taken from a stream, may give but little information as to its fitness for domestic use; and that, before deciding upon a proposed source for town supply, a much more comprehensive study, extending throughout the year, is imperative.

It is gratifying to note that "the Board has begun an investigation which it hopes to continue until the condition and liability of pollution of all important sources of public water supplies in Ohio, shall have been satisfactorily examined." Would that more states followed this excellent example!

The section, by Mr. Allen Hazen, devoted to "stream pollution," shows that most of the larger streams of the state are used for public supplies; that all of them receive a notable addition of sewage, and that the waters of such streams, below the sewage outfalls, are unwholesome.

Prof. N. W. Lord contributes a voluminous report upon the chemical examination of the waters of the Scioto, Olentangy, and Mahoning Rivers, which is followed by the bacteriological examination of the same waters by Prof. A. M. Bleile. Each of these investigators resorts to the graphic form to illustrate his results, a mode of presentation that is always acceptable and striking.

Prof. Lord's methods of analysis do not vary from those usually followed, with the exception of a slight change in the scheme for "required oxygen." It is his custom to produce a faint pink color with the standard permanganate at the outset, and the amount of the reagent so used is not counted in the determination, it being considered to represent what is required to oxidize ferrous salts and hydrogen sulphide present. This suggestion would seem to be a good one, but the thought presents itself that easily decomposable organic matter might be present that would vie with the inorganic salts in rapidity of action.

Prof. Bleile very properly lays stress upon the fact that comparative results are looked for, in the bacteriological examination, rather than an exact knowledge of the number of germs present; and he very ingenuously makes use of a filter-paper saturated with formalin and placed within the cover of the Petri dish, in order to arrest growth after a fixed time, and prevent the colonies from breaking down the medium while waiting for their turn to be counted. He makes use of a beef-peptone-agar just alkaline to phenolphthalein, which is a reaction distinctly more alkaline than the medium commonly employed.

A report follows on stream gaugings and sources of river pollution, by Prof. C. W. Brown, after which Prof. Edward Orton, state geologist, devotes considerable space to "The Rock Waters and Flowing Wells of Ohio," chiefly of geological interest.

A "water-shed" map of the state closes a report of decided interest and value. There is no index. W. P. MASON.

BOOKS RECEIVED.

The Practical Compounding of Oils, Tallow, and Grease, for Lubrication, etc. By an expert oil refiner. London: Scott, Greenwood & Co.; and New York: D. Van Nostrand Co. 1898. vii+96 pp. Price, $3.50.

Ueber einen gasanalytischen Apparat. Von O. Binder. Reprinted from Chemischen Industrie, *1898*, No. 22. 12 pp.

Ginseng, Its Nature and Culture. Bulletin No. 78, Kentucky Agricultural Experiment Station of the State College of Kentucky, Lexington, Ky. November, 1898. 34 pp., with ten full-page plates.

VOL. XXI. [FEBRUARY, 1899.] NO. 2.

THE JOURNAL

OF THE

AMERICAN CHEMICAL SOCIETY.

A NEW METHOD FOR THE DETERMINATION OF ZINC.

BY A. C. LANGMUIR.

Received October 22, 1898.

PRACTICALLY two methods only are in general use for the gravimetric determination of zinc. Of these, the carbonate method with its many imperfections is being displaced by the phosphate method, at least in this country.

With care the latter will yield excellent results. In our practice it is customary to use ammonium phosphate in place of the usual sodium salt,[1] and after the precipitation of the phosphate to destroy the slight excess of ammonia remaining after heating on the water-bath, by the cautious addition of dilute acetic acid. Under these conditions the filtrate is free from zinc.

Directly igniting the sulphide and filter, and weighing as oxide or sulphide, has been used, but is open to serious objection if the amount of zinc is at all large.

As far as we are aware no one has proposed the solution of the sulphide in nitric acid, the evaporation of the solution so obtained and the conversion of the residue to oxide by ignition. As a second precipitation and washing is avoided it is quicker than the carbonate or phosphate methods and is preferable to

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[1] Garrigues: This Journal, 19, 934.

the latter in that the impurities almost invariably present in the zinc precipitate may be easily determined and allowed for.

The sample of ore for analysis (one-half to one gram according to its zinc content) is dissolved and the metals precipitated by hydrogen sulphide separated by the usual methods. After expelling hydrogen sulphide, the solution is colored by bromine water, and the iron and any manganese present are separated by ammonia. The precipitate is dissolved in hydrochloric acid and the precipitation is repeated a second or third time if necessary.

If the ore is one which is known to be free from lime and magnesia the combined filtrates may be boiled down immediately with the addition of an excess of nitric acid to destroy chlorides and ammonium salts. After the removal of the chlorine, the solution is transferred to a weighed platinum dish, evaporated to dryness, ignited and weighed as oxide.

The troublesome filtration and washing of the zinc sulphide should be avoided if possible. In our opinion better results are obtained by the ferrocyanide titration of the solution of the unwashed sulphide than by any gravimetric method involving the filtration and *washing* of this precipitate[1].

The zinc is best precipitated as follows: Acidulate the warm ammoniacal filtrate from the iron with hydrochloric acid, add a few drops of sulphurous acid to neutralize the bromine set free, then three or four drops of methyl orange.[2] Neutralize with ammonia carefully and add ammonium sulphide drop by drop with constant stirring until a drop of the solution gives a dark coloration with a drop of dilute ferric chloride solution on a porcelain plate, showing a slight excess only of ammonium sulphide. The liquid is now warmed on the water-bath until the sulphide has settled and is filtered through a double ribbed filter. Under these conditions a clear filtrate is invariably obtained, but if washing is attempted the filtrate is frequently cloudy.

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[1] C. F. McKenna has suggested to the author that the addition of a little paper pulp to the solution prior to filtration will insure a clear filtrate. If some asbestos is stirred into a cloudy zinc filtrate and the solution passed again through the paper the filtrate will generally be clear. But in any case the slow washing of the precipitate exposes us to a loss through oxidation.

[2] The methyl orange used in exactly neutralizing the solution prior to the ferrocyanide titration and which slightly interferes with the delicacy of the end-reaction, may be readily destroyed after the acidulation by pouring into the beaker a little bromine vapor and stirring this in.

We therefore dissolve directly, without washing, in hot nitric acid (1 : 3) or in dilute hydrochloric acid if cobalt or nickel are present, and correct the weight of the oxide subsequently found for the small amounts of lime or magnesia present. It is well to make a qualitative test for these elements in the filtrate from the sulphide. If absent or in small amount the correction in the weight of the oxide may be omitted.

The solution is boiled down rapidly in a casserole with the addition of nitric acid to expel chlorides. When almost dry the contents are rinsed into a weighed platinum dish or crucible. The evaporation is continued on the water-bath or hot plate until dry, when the nitrate is ignited at the full heat of the Bunsen burner. As some zinc sulphate, which is always present, is not decomposed at this temperature, it is necessary to break up this compound by intense ignition over the blast-lamp. Any lumps should be first broken up by a blunt glass rod. Ammonium carbonate may be used but is liable to occasion some loss.

It may be possible, by igniting at a low heat, to weigh the zinc as sulphate, after evaporating with sulphuric acid. We are working on this now.

After weighing, the oxide is dissolved in hydrochloric acid and the small amount of iron always present thrown down with ammonia, ignited, brushed into the tared watch-glass in the balance and weighed directly. The filtrate is acidulated with hydrochloric acid, heated to boiling, and tested for sulphates with barium chloride. A slight precipitate will usually form but this may, in general, be neglected if the ignition has been properly performed. If in weighable amount it may be treated as in the case of the iron, calculated to sulphur trioxide, and together with the ferric oxide deducted from the weight of the impure oxide.

If lime or magnesia were present the filtrate from the iron should be divided into equal parts, one of which is tested for sulphates and the other for lime and magnesia by throwing out the zinc as sulphide, and testing the filtrate by the ordinary methods. As a rule this is unnecessary unless the lime or magnesia is present in large amounts, for the sulphide is precipitated in dilute solution and the amount of lime remaining in the unwashed sulphide would usually be very small.

The correction for impurities may seem tedious but in reality it is quickly carried out. Richards has found that zinc oxide obtained by the ignition of the nitrate contains a little occluded nitrogen. This would only amount to a few tenths of a milligram and may be neglected unless unusually accurate work is called for.

For the determination of zinc in alloys containing copper, tin, lead, iron, and zinc, dissolve in nitric acid, evaporate to dryness, and take up with nitric acid if tin be present. Filter and separate copper and lead simultaneously by electrolysis. The solution should contain five to ten cc. concentrated nitric acid in 150 to 200 cc. water. After removing and washing the electrodes carrying copper and lead the solution is evaporated to dryness in a weighed platinum dish and the residue ignited and weighed. Dissolve in hydrochloric acid and separate the usually small amount of iron present by ammonia. Ignite, weigh, and deduct from the weight of the zinc oxide. If nickel be present the weight of the combined oxides may be taken and the nickel afterwards determined, when the zinc may be found by difference.

Zinc in pure spelters is best determined by difference. In impure samples it is sometimes more convenient and equally accurate to determine zinc directly. Dissolve one-half gram in nitric acid and separate the lead electrolytically in a solution carrying ten per cent. nitric acid. Use the platinum cylinder in this case to collect the lead peroxide. Evaporate the solution to dryness in a weighed dish, ignite, and weigh. Dissolve in a little hydrochloric acid, reduce with two to three grams granulated zinc, add sulphuric acid to complete the reaction, dilute with ice water to one liter, and titrate with permanganate. Correct for the amount of iron found. If cadmium, arsenic, or other impurities were present in more than traces the above method would be inapplicable unless modified to include treatment by hydrogen sulphide.

We have not found time to make an extended series of tests of this method but, in numerous analyses of ores and the complete analysis of alloys in which in duplicate analyses the zinc was determined by the well-known methods, the author has convinced himself of the accuracy of the method.

LABORATORY OF RICKETTS AND BANKS,
NEW YORK.

BAUMÉ'S HYDROMETER—AMERICAN STANDARD.

Calculated by Sidney S. Emery.

Received October 17, 1898

For Liquids Heavier than Water, Sp. Gr. = $\frac{145}{145-{}^{\circ}\text{Bé}}$ at 60° F.

°Bé.	Sp. gr.	°Bé.	Sp. gr.	°Bé.	Sp. gr.	°Bé.	Sp. gr.
0.0	1.0000	.9	1.0276	.8	1.0569	.7	1.0878
.1	1.0007	4.0	1.0284	.9	1.0576	.8	1.0886
.2	1.0014	.1	1.0291	8.0	1.0584	.9	1.0894
.3	1.0021	.2	1.0298	.1	1.0592	12.0	1.0902
.4	1.0028	.3	1.0306	.2	1.0599	.1	1.0910
.5	1.0035	.4	1.0313	.3	1.0607	.2	1.0919
.6	1.0042	.5	1.0320	.4	1.0615	.3	1.0927
.7	1.0049	.6	1.0328	.5	1.0623	.4	1.0935
.8	1.0055	.7	1.0335	.6	1.0630	.5	1.0943
.9	1.0062	.8	1.0342	.7	1.0638	.6	1.0952
1.0	1.0069	.9	1.0350	.8	1.0646	.7	1.0960
.1	1.0076	5.0	1.0357	.9	1.0654	.8	1.0968
.2	1.0083	.1	1.0365	9.0	1.0662	.9	1.0977
.3	1.0090	.2	1.0372	.1	1.0670	13.0	1.0985
.4	1.0097	.3	1.0379	.2	1.0677	.1	1.0993
.5	1.0105	.4	1.0387	.3	1.0685	.2	1.1002
.6	1.0112	.5	1.0394	.4	1.0693	.3	1.1010
.7	1.0119	.6	1.0402	.5	1.0701	.4	1.1018
.8	1.0126	.7	1.0409	.6	1.0709	.5	1.1027
.9	1.0133	.8	1.0417	.7	1.0717	.6	1.1035
2.0	1.0140	.9	1.0424	.8	1.0725	.7	1.1043
.1	1.0147	6.0	1.0432	.9	1.0733	.8	1.1052
.2	1.0154	.1	1.0439	10.0	1.0741	.9	1.1060
.3	1.0161	.2	1.0447	.1	1.0749	14.0	1.1069
.4	1.0168	.3	1.0454	.2	1.0757	.1	1.1077
.5	1.0175	.4	1.0462	.3	1.0765	.2	1.1086
.6	1.0183	.5	1.0469	.4	1.0773	.3	1.1094
.7	1.0190	.6	1.0477	.5	1.0781	.4	1.1103
.8	1.0197	.7	1.0484	.6	1.0789	.5	1.1111
.9	1.0204	.8	1.0492	.7	1.0797	.6	1.1120
3.0	1.0211	.9	1.0500	.8	1.0805	.7	1.1128
.1	1.0218	7.0	1.0507	.9	1.0813	.8	1.1137
.2	1.0226	.1	1.0515	11.0	1.0821	.9	1.1145
.3	1.0233	.2	1.0522	.1	1.0829	15.0	1.1154
.4	1.0240	.3	1.0530	.2	1.0837	.1	1.1162
.5	1.0247	.4	1.0538	.3	1.0845	.2	1.1171
.6	1.0255	.5	1.0545	.4	1.0853	.3	1.1180
.7	1.0262	.6	1.0553	.5	1.0861	.4	1.1188
.8	1.0269	.7	1.0561	.6	1.0870	.5	1.1197

°Bé.	Sp. gr.	°Bé.	Sp. gr.	°Bé.	Sp. gr.	°Bé.	Sp. gr.
.6	1.1206	.2	1.1619	.8	1.2063	.4	1.2543
.7	1.1214	.3	1.1628	.9	1.2073	.5	1.2554
.8	1.1223	.4	1.1637	25.0	1.2083	.6	1.2565
.9	1.1232	.5	1.1647	.1	1.2093	.7	1.2576
16.0	1.1240	.6	1.1656	.2	1.2104	.8	1.2587
.1	1.1249	.7	1.1665	.3	1.2114	.9	1.2598
.2	1.1258	.8	1.1675	.4	1.2124	30.0	1.2609
.3	1.1267	.9	1.1684	.5	1.2134	.1	1.2620
.4	1.1275	21.0	1.1694	.6	1.2144	.2	1.2631
.5	1.1284	.1	1.1703	.7	1.2154	.3	1.2642
.6	1.1293	.2	1.1712	.8	1.2164	.4	1.2653
.7	1.1302	.3	1.1722	.9	1.2175	.5	1.2664
.8	1.1310	.4	1.1731	26.0	1.2185	.6	1.2675
.9	1.1319	.5	1.1741	.1	1.2195	.7	1.2686
17.0	1.1328	.6	1.1750	.2	1.2205	.8	1.2697
.1	1.1337	.7	1.1760	.3	1.2216	.9	1.2708
.2	1.1346	.8	1.1769	.4	1.2226	31.0	1.2719
.3	1.1355	.9	1.1779	.5	1.2236	.1	1.2730
.4	1.1364	22.0	1.1789	.6	1.2247	.2	1.2742
.5	1.1373	.1	1.1798	.7	1.2257	.3	1.2753
.6	1.1381	.2	1.1808	.8	1.2267	.4	1.2764
.7	1.1390	.3	1.1817	.9	1.2278	.5	1.2775
.8	1.1399	.4	1.1827	27.0	1.2288	.6	1.2787
.9	1.1408	.5	1.1837	.1	1.2299	.7	1.2798
18.0	1.1417	.6	1.1846	.2	1.2309	.8	1.2809
.1	1.1426	.7	1.1856	.3	1.2319	.9	1.2821
.2	1.1435	.8	1.1866	.4	1.2330	32.0	1.2832
.3	1.1444	.9	1.1876	.5	1.2340	.1	1.2843
.4	1.1453	23.0	1.1885	.6	1.2351	.2	1.2855
.5	1.1462	.1	1.1895	.7	1.2361	.3	1.2866
.6	1.1472	.2	1.1905	.8	1.2372	.4	1.2877
.7	1.1481	.3	1.1915	.9	1.2383	.5	1.2889
.8	1.1490	.4	1.1924	28.0	1.2393	.6	1.2900
.9	1.1499	.5	1.1934	.1	1.2404	.7	1.2912
19.0	1.1508	.6	1.1944	.2	1.2414	.8	1.2923
.1	1.1517	.7	1.1954	.3	1.2425	.9	1.2935
.2	1.1526	.8	1.1964	.4	1.2436	33.0	1.2946
.3	1.1535	.9	1.1974	.5	1.2446	.1	1.2958
.4	1.1545	24.0	1.1983	.6	1.2457	.2	1.2970
.5	1.1554	.1	1.1993	.7	1.2468	.3	1.2981
.6	1.1563	.2	1.2003	.8	1.2478	.4	1.2993
.7	1.1572	.3	1.2013	.9	1.2489	.5	1.3004
.8	1.1581	.4	1.2023	29.0	1.2500	.6	1.3016
.9	1.1591	.5	1.2033	.1	1.2511	.7	1.3028
20.0	1.1600	.6	1.2043	.2	1.2522	.8	1.3040
.1	1.1609	.7	1.2053	.3	1.2532	.9	1.3051

°Bé.	Sp. gr.	°Bé.	Sp. gr.	°Bé.	Sp. gr.	°Bé.	Sp. gr.
34.0	1.3063	.6	1.3628	.2	1.4244	.8	1.4918
.1	1.3075	.7	1.3641	.3	1.4258	.9	1.4933
.2	1.3087	.8	1.3653	.4	1.4272	48.0	1.4948
.3	1.3098	.9	1.3666	.5	1.4286	.1	1.4964
.4	1.3110	39.0	1.3679	.6	1.4300	.2	1.4979
.5	1.3122	.1	1.3692	.7	1.4314	.3	1.4995
.6	1.3134	.2	1.3705	.8	1.4328	.4	1.5010
.7	1.3146	.3	1.3718	.9	1.4342	.5	1.5026
.8	1.3158	.4	1.3731	44.0	1.4356	.6	1.5041
.9	1.3170	.5	1.3744	.1	1.4371	.7	1.5057
35.0	1.3182	.6	1.3757	.2	1.4385	.8	1.5073
.1	1.3194	.7	1.3770	.3	1.4399	.9	1.5088
.2	1.3206	.8	1.3783	.4	1.4414	49.0	1.5104
.3	1.3218	.9	1.3796	.5	1.4428	.1	1.5120
.4	1.3230	40.0	1.3810	.6	1.4442	.2	1.5136
.5	1.3242	.1	1.3823	.7	1.4457	.3	1.5152
.6	1.3254	.2	1.3836	.8	1.4471	.4	1.5167
.7	1.3266	.3	1.3849	.9	1.4486	.5	1.5183
.8	1.3278	.4	1.3862	45.0	1.4500	.6	1.5199
.9	1.3291	.5	1.3876	.1	1.4515	.7	1.5215
36.0	1.3303	.6	1.3889	.2	1.4529	.8	1.5231
.1	1.3315	.7	1.3902	.3	1.4544	.9	1.5247
.2	1.3327	.8	1.3916	.4	1.4558	50.0	1.5263
.3	1.3339	.9	1.3929	.5	1.4573	.1	1.5279
.4	1.3352	41.0	1.3942	.6	1.4588	.2	1.5295
.5	1.3364	.1	1.3956	.7	1.4602	.3	1.5312
.6	1.3376	.2	1.3969	.8	1.4617	.4	1.5328
.7	1.3389	.3	1.3983	.9	1.4632	.5	1.5344
.8	1.3401	.4	1.3996	46.0	1.4646	.6	1.5360
.9	1.3414	.5	1.4010	.1	1.4661	.7	1.5376
37.0	1.3426	.6	1.4023	.2	1.4676	.8	1.5393
.1	1.3438	.7	1.4037	.3	1.4691	.9	1.5409
.2	1.3451	.8	1.4050	.4	1.4706	51.0	1.5426
.3	1.3463	.9	1.4064	.5	1.4721	.1	1.5442
.4	1.3476	42.0	1.4078	.6	1.4736	.2	1.5458
.5	1.3488	.1	1.4091	.7	1.4751	.3	1.5475
.6	1.3501	.2	1.4105	.8	1.4766	.4	1.5491
.7	1.3514	.3	1.4119	.9	1.4781	.5	1.5508
.8	1.3526	.4	1.4133	47.0	1.4796	.6	1.5525
.9	1.3539	.5	1.4146	.1	1.4811	.7	1.5541
38.0	1.3551	.6	1.4160	.2	1.4826	.8	1.5558
.1	1.3564	.7	1.4174	.3	1.4841	.9	1.5575
.2	1.3577	.8	1.4188	.4	1.4857	52.0	1.5591
.3	1.3590	.9	1.4202	.5	1.4872	.1	1.5608
.4	1.3602	43.0	1.4216	.6	1.4887	.2	1.5625
.5	1.3615	.1	1.4230	.7	1.4902	.3	1.5642

°Bé.	Sp. gr.	°Bé.	Sp. gr.	°Bé.	Sp. gr.	°Bé.	Sp. gr.
.4	1.5659	.8	1.6440	.2	1.7303	.6	1.8262
.5	1.5676	.9	1.6459	.3	1.7324	.7	1.8285
.6	1.5693	57.0	1.6477	.4	1.7344	.8	1.8308
.7	1.5710	.1	1.6496	.5	1.7365	.9	1.8331
.8	1.5727	.2	1.6515	.6	1.7386	66.0	1.8354
.9	1.5744	.3	1.6534	.7	1.7407	.1	1.8378
53.0	1.5761	.4	1.6553	.8	1.7428	.2	1.8401
.1	1.5778	.5	1.6571	.9	1.7449	.3	1.8424
.2	1.5795	.6	1.6590	62.0	1.7470	.4	1.8448
.3	1.5812	.7	1.6609	.1	1.7491	.5	1.8471
.4	1.5830	.8	1.6628	.2	1.7512	.6	1.8495
.5	1.5847	.9	1.6648	.3	1.7533	.7	1.8519
.6	1.5864	58.0	1.6667	.4	1.7554	.8	1.8542
.7	1.5882	.1	1.6686	.5	1.7576	.9	1.8566
.8	1.5899	.2	1.6705	.6	1.7597	67.0	1.8590
.9	1.5917	.3	1.6724	.7	1.7618	.1	1.8614
54.0	1.5934	.4	1.6744	.8	1.7640	.2	1.8638
.1	1.5952	.5	1.6763	.9	1.7661	.3	1.8662
.2	1.5969	.6	1.6782	63.0	1.7683	.4	1.8686
.3	1.5987	.7	1.6802	.1	1.7705	.5	1.8710
.4	1.6004	.8	1.6821	.2	1.7726	.6	1.8734
.5	1.6022	.9	1.6841	.3	1.7748	.7	1.8758
.6	1.6040	59.0	1.6860	.4	1.7770	.8	1.8782
.7	1.6058	.1	1.6880	.5	1.7791	.9	1.8807
.8	1.6075	.2	1.6900	.6	1.7813	68.0	1.8831
.9	1.6093	.3	1.6919	.7	1.7835	.1	1.8856
55.0	1.6111	.4	1.6939	.8	1.7857	.2	1.8880
.1	1.6129	.5	1.6959	.9	1.7879	.3	1.8905
.2	1.6147	.6	1.6979	64.0	1.7901	.4	1.8930
.3	1.6165	.7	1.6999	.1	1.7923	.5	1.8954
.4	1.6183	.8	1.7019	.2	1.7946	.6	1.8979
.5	1.6201	.9	1.7039	.3	1.7968	.7	1.9004
.6	1.6219	60.0	1.7059	.4	1.7990	.8	1.9029
.7	1.6237	.1	1.7079	.5	1.8012	.9	1.9054
.8	1.6256	.2	1.7099	.6	1.8035	69.0	1.9079
.9	1.6274	.3	1.7119	.7	1.8057	.1	1.9104
56.0	1.6292	.4	1.7139	.8	1.8080	.2	1.9129
.1	1.6310	.5	1.7160	.9	1.8102	.3	1.9155
.2	1.6329	.6	1.7180	65.0	1.8125	.4	1.9180
.3	1.6347	.7	1.7200	.1	1.8148	.5	1.9205
.4	1.6366	.8	1.7221	.2	1.8170	.6	1.9231
.5	1.6384	.9	1.7241	.3	1.8193	.7	1.9256
.6	1.6403	61.0	1.7262	.4	1.8216	.8	1.9282
.7	1.6421	.1	1.7282	.5	1.8239	.9	1.9308
						70.0	1.9333

°Bé.	Sp. gr.	°Bé.	Sp. gr.	°Bé.	Sp. gr.	°Bé.	Sp. gr
0	1.0000	6/8	1.0413	4/8	1.0861	2/8	1.1350
1/8	1.0009	7/8	1.0422	5/8	1.0872	3/8	1.1361
2/8	1.0017	6	1.0432	6/8	1.0882	4/8	1.1373
3/8	1.0026	1/8	1.0441	7/8	1.0892	5/8	1.1384
4/8	1.0035	2/8	1.0450	12	1.0902	6/8	1.1395
5/8	1.0043	3/8	1.0460	1/8	1.0913	7/8	1.1406
6/8	1.0052	4/8	1.0469	2/8	1.0923	18	1.1417
7/8	1.0061	5/8	1.0479	3/8	1.0933	1/8	1.1428
1	1.0069	6/8	1.0488	4/8	1.0943	2/8	1.1440
1/8	1.0078	7/8	1.0498	5/8	1.0954	3/8	1.1451
2/8	1.0087	7	1.0507	6/8	1.0964	4/8	1.1462
3/8	1.0096	1/8	1.0517	7/8	1.0974	5/8	1.1474
4/8	1.0105	2/8	1.0526	13	1.0985	6/8	1.1485
5/8	1.0113	3/8	1.0536	1/8	1.0995	7/8	1.1496
6/8	1.0122	4/8	1.0545	2/8	1.1006	19	1.1508
7/8	1.0131	5/8	1.0555	3/8	1.1016	1/8	1.1519
2	1.0140	6/8	1.0565	4/8	1.1027	2/8	1.1531
1/8	1.0149	7/8	1.0574	5/8	1.1037	3/8	1.1542
2/8	1.0158	8	1.0584	6/8	1.1048	4/8	1.1554
3/8	1.0167	1/8	1.0594	7/8	1.1058	5/8	1.1565
4/8	1.0175	2/8	1.0603	14	1.1069	6/8	1.1577
5/8	1.0184	3/8	1.0613	1/8	1.1079	7/8	1.1588
6/8	1.0193	4/8	1.0623	2/8	1.1090	20	1.1600
7/8	1.0202	5/8	1.0632	3/8	1.1100	1/8	1.1612
3	1.0211	6/8	1.0642	4/8	1.1111	2/8	1.1623
1/8	1.0220	7/8	1.0652	5/8	1.1122	3/8	1.1635
2/8	1.0229	9	1.0662	6/8	1.1132	4/8	1.1647
3/8	1.0238	1/8	1.0672	7/8	1.1143	5/8	1.1658
4/8	1.0247	2/8	1.0681	15	1.1154	6/8	1.1670
5/8	1.0256	3/8	1.0691	1/8	1.1165	7/8	1.1682
6/8	1.0265	4/8	1.0701	2/8	1.1175	21	1.1694
7/8	1.0275	5/8	1.0711	3/8	1.1186	1/8	1.1705
4	1.0284	6/8	1.0721	4/8	1.1197	2/8	1.1717
1/8	1.0293	7/8	1.0731	5/8	1.1208	3/8	1.1729
2/8	1.0302	10	1.0741	6/8	1.1219	4/8	1.1741
3/8	1.0311	1/8	1.0751	7/8	1.1229	5/8	1.1753
4/8	1.0320	2/8	1.0761	16	1.1240	6/8	1.1765
5/8	1.0329	3/8	1.0771	1/8	1.1251	7/8	1.1777
6/8	1.0339	4/8	1.0781	2/8	1.1262	22	1.1789
7/8	1.0348	5/8	1.0791	3/8	1.1273	1/8	1.1801
5	1.0357	6/8	1.0801	4/8	1.1284	2/8	1.1813
1/8	1.0366	7/8	1.0811	5/8	1.1295	3/8	1.1825
2/8	1.0376	11	1.0821	6/8	1.1306	4/8	1.1837
3/8	1.0385	1/8	1.0831	7/8	1.1317	5/8	1.1849
4/8	1.0394	2/8	1.0841	17	1.1328	6/8	1.1861
5/8	1.0404	3/8	1.0851	1/8	1.1339	7/8	1.1873

°Bé.	Sp. gr.	°Bé.	Sp. gr.	°Bé.	Sp. gr.	°Bé.	Sp. gr.
23	1.1885	¾	1.2473	½	1.3122	¼	1.3843
⅛	1.1897	⅞	1.2487	⅝	1.3137	⅜	1.3859
¼	1.1910	29	1.2500	¾	1.3152	½	1.3876
⅜	1.1922	⅛	1.2513	⅞	1.3167	⅝	1.3892
½	1.1934	¼	1.2527	35	1.3182	¾	1.3909
⅝	1.1946	⅜	1.2541	⅛	1.3197	⅞	1.3926
¾	1.1959	½	1.2554	¼	1.3212	41	1.3942
⅞	1.1971	⅝	1.2568	⅜	1.3227	⅛	1.3959
24	1.1983	¾	1.2581	½	1.3242	¼	1.3976
⅛	1.1996	⅞	1.2595	⅝	1.3257	⅜	1.3993
¼	1.2008	30	1.2609	¾	1.3272	½	1.4010
⅜	1.2021	⅛	1.2622	⅞	1.3288	⅝	1.4027
½	1.2033	¼	1.2636	36	1.3303	¾	1.4044
⅝	1.2046	⅜	1.2650	⅛	1.3318	⅞	1.4061
¾	1.2058	½	1.2664	¼	1.3333	42	1.4078
⅞	1.2071	⅝	1.2678	⅜	1.3349	⅛	1.4095
25	1.2083	¾	1.2691	½	1.3364	¼	1.4112
⅛	1.2096	⅞	1.2705	⅝	1.3379	⅜	1.4129
¼	1.2109	31	1.2719	¾	1.3395	½	1.4146
⅜	1.2121	⅛	1.2733	⅞	1.3410	⅝	1.4164
½	1.2134	¼	1.2747	37	1.3426	¾	1.4181
⅝	1.2147	⅜	1.2761	⅛	1.3441	⅞	1.4198
¾	1.2159	½	1.2775	¼	1.3457	43	1.4216
⅞	1.2172	⅝	1.2789	⅜	1.3473	⅛	1.4233
26	1.2185	¾	1.2804	½	1.3488	¼	1.4251
⅛	1.2198	⅞	1.2818	⅝	1.3504	⅜	1.4268
¼	1.2211	32	1.2832	¾	1.3520	½	1.4286
⅜	1.2223	⅛	1.2846	⅞	1.3536	⅝	1.4303
½	1.2236	¼	1.2860	38	1.3551	¾	1.4321
⅝	1.2249	⅜	1.2875	⅛	1.3567	⅞	1.4339
¾	1.2262	½	1.2889	¼	1.3583	44	1.4356
⅞	1.2275	⅝	1.2903	⅜	1.3599	⅛	1.4374
27	1.2288	¾	1.2918	½	1.3615	¼	1.4392
⅛	1.2301	⅞	1.2932	⅝	1.3631	⅜	1.4410
¼	1.2314	33	1.2946	¾	1.3647	½	1.4428
⅜	1.2327	⅛	1.2961	⅞	1.3663	⅝	1.4446
½	1.2340	¼	1.2975	39	1.3679	¾	1.4464
⅝	1.2354	⅜	1.2990	⅛	1.3695	⅞	1.4482
¾	1.2367	½	1.3004	¼	1.3712	45	1.4500
⅞	1.2380	⅝	1.3019	⅜	1.3728	⅛	1.4518
28	1.2393	¾	1.3034	½	1.3744	¼	1.4537
⅛	1.2406	⅞	1.3048	⅝	1.3760	⅜	1.4555
¼	1.2420	34	1.3063	¾	1.3777	½	1.4573
⅜	1.2433	⅛	1.3078	⅞	1.3793	⅝	1.4591
½	1.2446	¼	1.3093	40	1.3810	¾	1.4610
⅝	1.2460	⅜	1.3107	⅛	1.3826	⅞	1.4628

°Bé.	Sp. gr.	°Bé.	Sp. gr.	°Bé.	Sp. gr.	°Bé.	Sp. gr.
46	1.4646	6/8	1.5550	4/8	1.6571	2/8	1.7737
1/8	1.4665	7/8	1.5570	5/8	1.6595	3/8	1.7764
2/8	1.4684	52	1.5591	6/8	1.6619	4/8	1.7791
3/8	1.4702	1/8	1.5612	7/8	1.6643	5/8	1.7819
4/8	1.4721	2/8	1.5633	58	1.6667	6/8	1.7846
5/8	1.4739	3/8	1.5655	1/8	1.6691	7/8	1.7874
6/8	1.4758	4/8	1.5676	2/8	1.6715	64	1.7901
7/8	1.4777	5/8	1.5697	3/8	1.6739	1/8	1.7929
47	1.4796	6/8	1.5718	4/8	1.6763	2/8	1.7957
1/8	1.4815	7/8	1.5739	5/8	1.6787	3/8	1.7984
2/8	1.4834	53	1.5761	6/8	1.6812	4/8	1.8012
3/8	1.4853	1/8	1.5782	7/8	1.6836	5/8	1.8040
4/8	1.4872	2/8	1.5804	59	1.6860	6/8	1.8069
5/8	1.4891	3/8	1.5825	1/8	1.6885	7/8	1.8097
6/8	1.4910	4/8	1.5847	2/8	1.6910	65	1.8125
7/8	1.4929	5/8	1.5869	3/8	1.6934	1/8	1.8153
48	1.4948	6/8	1.5890	4/8	1.6959	2/8	1.8182
1/8	1.4968	7/8	1.5912	5/8	1.6984	3/8	1.8210
2/8	1.4987	54	1.5934	6/8	1.7009	4/8	1.8239
3/8	1.5006	1/8	1.5956	7/8	1.7034	5/8	1.8268
4/8	1.5026	2/8	1.5978	60	1.7059	6/8	1.8297
5/8	1.5045	3/8	1.6000	1/8	1.7084	7/8	1.8325
6/8	1.5065	4/8	1.6022	2/8	1.7109	66	1.8354
7/8	1.5085	5/8	1.6044	3/8	1.7134	1/8	1.8383
49	1.5104	6/8	1.6066	4/8	1.7160	2/8	1.8413
1/8	1.5124	7/8	1.6089	5/8	1.7185	3/8	1.8442
2/8	1.5144	55	1.6111	6/8	1.7211	4/8	1.8471
3/8	1.5163	1/8	1.6134	7/8	1.7236	5/8	1.8501
4/8	1.5183	2/8	1.6156	61	1.7262	6/8	1.8530
5/8	1.5203	3/8	1.6179	1/8	1.7288	7/8	1.8560
6/8	1.5223	4/8	1.6201	2/8	1.7313	67	1.8590
7/8	1.5243	5/8	1.6224	3/8	1.7339	1/8	1.8620
50	1.5263	6/8	1.6246	4/8	1.7365	2/8	1.8650
1/8	1.5283	7/8	1.6269	5/8	1.7391	3/8	1.8680
2/8	1.5303	56	1.6292	6/8	1.7417	4/8	1.8710
3/8	1.5324	1/8	1.6315	7/8	1.7444	5/8	1.8740
4/8	1.5344	2/8	1.6338	62	1.7470	6/8	1.8770
5/8	1.5364	3/8	1.6361	1/8	1.7496	7/8	1.8801
6/8	1.5385	4/8	1.6384	2/8	1.7523	68	1.8831
7/8	1.5405	5/8	1.6407	3/8	1.7549	1/8	1.8862
51	1.5426	6/8	1.6431	4/8	1.7576	2/8	1.8893
1/8	1.5446	7/8	1.6454	5/8	1.7602	3/8	1.8923
2/8	1.5467	57	1.6477	6/8	1.7629	4/8	1.8954
3/8	1.5487	1/8	1.6501	7/8	1.7656	5/8	1.8985
4/8	1.5508	2/8	1.6524	63	1.7683	6/8	1.9016
5/8	1.5529	3/8	1.6548	1/8	1.7710	7/8	1.9048

°Bé.	Sp. gr.	°Bé.	Sp. gr.	°Bé.	Sp. gr.	°Bé.	Sp. gr.
69	1.9079	$\frac{3}{8}$	1.9174	$\frac{5}{8}$	1.9237	$\frac{7}{8}$	1.9301
$\frac{1}{8}$	1.9110	$\frac{4}{8}$	1.9205	$\frac{6}{8}$	1.9269	70	1.9333
$\frac{2}{8}$	1.9142						

For Liquids Lighter than Water, Sp. Gr. $= \frac{140}{130 + {}^{\circ}\text{Bé}}$ at 60° F.

°Bé.	Sp. gr.	°Bé.	Sp. gr.	°Bé.	Sp. gr.	°Bé.	Sp. gr.
10.0	1.0000	.9	0.9729	.8	0.9472	.7	0.9229
.1	0.9993	14.0	0.9722	.9	0.9466	.8	0.9223
.2	0.9986	.1	0.9715	18.0	0.9459	.9	0.9217
.3	0.9979	.2	0.9709	.1	0.9453	22.0	0.9211
.4	0.9972	.3	0.9702	.2	0.9447	.1	0.9204
.5	0.9964	.4	0.9695	.3	0.9440	.2	0.9198
.6	0.9957	.5	0.9689	.4	0.9434	.3	0.9192
.7	0.9950	.6	0.9682	.5	0.9428	.4	0.9186
.8	0.9943	.7	0.9675	.6	0.9421	.5	0.9180
.9	0.9936	.8	0.9669	.7	0.9415	.6	0.9174
11.0	0.9929	.9	0.9662	.8	0.9409	.7	0.9168
.1	0.9922	15.0	0.9655	.9	0.9402	.8	0.9162
.2	0.9915	.1	0.9649	19.0	0.9396	.9	0.9156
.3	0.9908	.2	0.9642	.1	0.9390	23.0	0.9150
.4	0.9901	.3	0.9635	.2	0.9383	.1	0.9144
.5	0.9894	.4	0.9629	.3	0.9377	.2	0.9138
.6	0.9887	.5	0.9622	.4	0.9371	.3	0.9132
.7	0.9880	.9	0.9615	.5	0.9365	.4	0.9126
.8	0.9873	.7	0.9609	.6	0.9358	.5	0.9121
.9	0.9866	.8	0.9602	.7	0.9352	.6	0.9115
12.0	0.9859	.9	0.9596	.8	0.9346	.7	0.9109
.1	0.9852	16.0	0.9589	.9	0.9340	.8	0.9103
.2	0.9845	.1	0.9582	20.0	0.9333	.9	0.9097
.3	0.9838	.2	0.0576	.1	0.9327	24.0	0.9091
.4	0.9831	.3	0.9569	.2	0.9321	.1	0.9085
.5	0.9825	.4	0.9563	.3	0.9315	.2	0.9079
.6	0.9818	.5	0.9556	.4	0.9309	.3	0.9073
.7	0.9811	.6	0.9550	.5	0.9302	.4	0.9067
.8	0.9804	.7	0.9543	.6	0.9296	.5	0.9061
.9	0.9797	.8	0.9537	.7	0.9290	.6	0.9056
13.0	0.9790	.9	0.9530	.8	0.9284	.7	0.9050
.1	0.9783	17.0	0.9524	.9	0.9278	.8	0.9044
.2	0.9777	.1	0.9517	21.0	0.9272	.9	0.9038
.3	0.9770	.2	0.9511	.1	0.9265	25.0	0.9032
.4	0.9763	.3	0.9504	.2	0.9259	.1	0.9026
.5	0.9756	.4	0.9498	.3	0.9253	.2	0.9021
.6	0.9749	.5	0.9492	.4	0.9247	.3	0.9015
.7	0.9743	.6	0.9485	.5	0.9241	.4	0.9009
.8	0.9736	.7	0.9479	.6	0.9235	.5	0.9003

°Bé.	Sp. gr.	°Bé.	Sp. gr.	°Bé.	Sp. gr.	°Bé.	Sp. gr.
.6	0.8997	.2	0.8739	.8	0.8495	.4	0.8264
.7	0.8992	.3	0.8734	.9	0.8490	.5	0.8260
.8	0.8986	.4	0.8728	35.0	0.8485	.6	0.8255
.9	0.8980	.5	0.8723	.1	0.8480	.7	0.8250
26.0	0.8974	.6	0.8717	.2	0.8475	.8	0.8245
.1	0.8969	.7	0.8712	.3	0.8469	.9	0.8240
.2	0.8963	.8	0.8706	.4	0.8464	40.0	0.8235
.3	0.8957	.9	0.8701	.5	0.8459	.1	0.8230
.4	0.8951	31.0	0.8696	.6	0.8454	.2	0.8226
.5	0.8946	.1	0.8690	.7	0.8449	.3	0.8221
.6	0.8940	.2	0.8685	.8	0.8444	.4	0.8216
.7	0.8934	.3	0.8679	.9	0.8439	.5	0.8211
.8	0.8929	.4	0.8674	36.0	0.8434	.6	0.8206
.9	0.8923	.5	0.8669	.1	0.8429	.7	0.8202
27.0	0.8917	.6	0.8663	.2	0.8424	.8	0.8197
.1	0.8912	.7	0.8658	.3	0.8418	.9	0.8192
.2	0.8906	.8	0.8653	.4	0.8413	41.0	0.8187
.3	0.8900	.9	0.8647	.5	0.8408	.1	0.8182
.4	0.8895	32.0	0.8642	.6	0.8403	.2	0.8178
.5	0.8889	.1	0.8637	.7	0.8398	.3	0.8173
.6	0.8883	.2	0.8631	.8	0.8393	.4	0.8168
.7	0.8878	.3	0.8626	.9	0.8388	.5	0.8163
.8	0.8872	.4	0.8621	37.0	0.8383	.6	0.8159
.9	0.8866	.5	0.8615	.1	0.8378	.7	0.8154
28.0	0.8861	.6	0.8610	.2	0.8373	.8	0.8149
.1	0.8855	.7	0.8605	.3	0.8368	.9	0.8144
.2	0.8850	.8	0.8600	.4	0.8363	42.0	0.8140
.3	0.8844	.9	0.8594	.5	0.8358	.1	0.8135
.4	0.8838	33.0	0.8589	.6	0.8353	.2	0.8130
.5	0.8833	.1	0.8584	.7	0.8348	.3	0.8125
.6	0.8821	.2	0.8578	.8	0.8343	.4	0.8121
.7	0.8822	.3	0.8573	.9	0.8338	.5	0.8116
.8	0.8816	.4	0.8568	38.0	0.8333	.6	0.8111
.9	0.8811	.5	0.8563	.1	0.8328	.7	0.8107
29.0	0.8805	.6	0.8557	.2	0.8323	.8	0.8102
.1	0.8799	.7	0.8552	.3	0.8318	.9	0.8097
.2	0.8794	.8	0.8547	.4	0.8314	43.0	0.8092
.3	0.8788	.9	0.8542	.5	0.8309	.1	0.8088
.4	0.8783	34.0	0.8537	.6	0.8304	.2	0.8083
.5	0.8777	.1	0.8531	.7	0.8299	.3	0.8078
.6	0.8772	.2	0.8526	.8	0.8294	.4	0.8074
.7	0.8766	.3	0.8521	.9	0.8289	.5	0.8069
.8	0.8761	.4	0.8516	39.0	0.8284	.6	0.8065
.9	0.8755	.5	0.8511	.1	0.8279	.7	0.8060
30.0	0.8750	.6	0.8505	.2	0.8274	.8	0.8055
.1	0.8745	.7	0.8500	.3	0.8269	.9	0.8051

°Bé.	Sp. gr.	°Bé.	Sp. gr.	°Bé.	Sp. gr.	°Bé.	Sp. gr.
44.0	0.8046	.6	0.7839	.2	0.7642	.8	0.7455
.1	0.8041	.7	0.7834	.3	0.7638	.9	0.7451
.2	0.8037	.8	0.7830	.4	0.7634	58.0	0.7447
.3	0.8032	.9	0.7826	.5	0.7629	.1	0.7443
.4	0.8028	49.0	0.7821	.6	0.7625	.2	0.7439
.5	0.8023	.1	0.7817	.7	0.7621	.3	0.7435
.6	0.8018	.2	0.7812(5)	.8	0.7617	.4	0.7431
.7	0.8014	.3	0.7808	.9	0.7613	.5	0.7427
.8	0.8009	.4	0.7804	54.0	0.7609	.6	0.7423
.9	0.8005	.5	0.7799	.1	0.7605	.7	0.7419
45.0	0.8000	.6	0.7795	.2	0.7600	.8	0.7415
.1	0.7995	.7	0.7791	.3	0.7596	.9	0.7411
.2	0.7991	.8	0.7786	.4	0.7592	59.0	0.7407
.3	0.7986	.9	0.7782	.5	0.7588	.1	0.7403
.4	0.7982	50.0	0.7778	.6	0.7584	.2	0.7400
.5	0.7977	.1	0.7773	.7	0.7580	.3	0.7396
.6	0.7973	.2	0.7769	.8	0.7576	.4	0.7392
.7	0.7968	.3	0.7765	.9	0.7572	.5	0.7388
.8	0.7964	.4	0.7761	55.0	0.7568	.6	0.7384
.9	0.7959	.5	0.7756	.1	0.7563	.7	0.7380
46.0	0.7955	.6	0.7752	.2	0.7559	.8	0.7376
.1	0.7950	.7	0.7748	.3	0.7555	.9	0.7372
.2	0.7946	.8	0.7743	.4	0.7551	60.0	0.7368
.3	0.7941	.9	0.7739	.5	0.7547	.1	0.7365
.4	0.7937	51.0	0.7735	.6	0.7543	.2	0.7361
.5	0.7932	.1	0.7731	.7	0.7539	.3	0.7357
.6	0.7928	.2	0.7726	.8	0.7535	.4	0.7353
.7	0.7923	.3	0.7722	.9	0.7531	.5	0.7349
.8	0.7919	.4	0.7718	56.0	0.7527	.8	0.7345
.9	0.7914	.5	0.7713	.1	0.7523	.7	0.7341
47.0	0.7910	.6	0.7709	.2	0.7519	.8	0.7338
.1	0.7905	.7	0.7705	.3	0.7515	.9	0.7334
.2	0.7901	.8	0.7701	.4	0.7511	61.0	0.7330
.3	0.7896	.9	0.7697	.5	0.7507	.1	0.7326
.4	0.7892	52.0	0.7692	.6	0.7503	.2	0.7322
.5	0.7887	.1	0.7688	.7	0.7499	.3	0.7318
.6	0.7883	.2	0.7684	.8	0.7495	.4	0.7315
.7	0.7878	.3	0.7680	.9	0.7491	.5	0.7311
.8	0.7874	.4	0.7675	57.0	0.7487	.6	0.7307
.9	0.7870	.5	0.7671	.1	0.7483	.7	0.7303
48.0	0.7865	.6	0.7667	.2	0.7479	.8	0.7299
.1	0.7861	.7	0.7663	.3	0.7475	.9	0.7295
.2	0.7856	.8	0.7659	.4	0.7471	62.0	0.7292
.3	0.7852	.9	0.7654	.5	0.7467	.1	0.7288
.4	0.7848	53.0	0.7650	.6	0.7463	.2	0.7284
.5	0.7843	.1	0.7646	.7	0.7459	.3	0.7280

°Bé.	Sp. gr.	°Bé.	Sp. gr.	°Bé.	Sp. gr.	°Bé.	Sp. gr.
.4	0.7277	.9	0.7110	.3	0.6955	.7	0.6806
.5	0.7273	67.0	0.7107	.4	0.6951	.8	0.6803
.6	0.7269	.1	0.7103	.5	0.6948	.9	0.6799
.7	0.7265	.2	0.7099	.6	0.6944	76.0	0.6796
.8	0.7261	.3	0.7096	.7	0.6941	.1	0.6793
.9	0.7258	.4	0.7092	.8	0.6938	.2	0.6790
63.0	0.7254	.5	0.7089	.9	0.6934	.3	0.6786
.1	0.7250	.6	0.7085	72.0	0.6931	.4	0.6783
.2	0.7246	.7	0.7081	.1	0.6927	.5	0.6780
.3	0.7243	.8	0.7078	.2	0.6924	.6	0.6776
.4	0.7239	.9	0.7074	.3	0.6920	.7	0.6773
.5	0.7235	68.0	0.7071	.4	0.6917	.8	0.6770
.6	0.7231	.1	0.7067	.5	0.6914	.9	0.6767
.7	0.7228	.2	0.7064	.6	0.6910	77.0	0.6763
.8	0.7224	.3	0.7060	.7	0.6907	.1	0.6760
.9	0.7220	.4	0.7056	.8	0.6903	.2	0.6757
64.0	0.7216	.5	0.7053	.9	0.6900	.3	0.6753
.1	0.7213	.6	0.7049	73.0	0.6897	.4	0.6750
.2	0.7209	.7	0.7046	.1	0.6893	.5	0.6747
.3	0.7205	.8	0.7042	.2	0.6890	.6	0.6744
.4	0.7202	.9	0.7039	.3	0.6886	.7	0.6740
.5	0.7198	69.0	0.7035	.4	0.6883	.8	0.6737
.6	0.7194	.1	0.7032	.5	0.6880	.9	0.6734
.7	0.7191	.2	0.7028	.6	0.6876	78.0	0.6731
.8	0.7187	.3	0.7025	.7	0.6873	.1	0.6728
.9	0.7183	.4	0.7021	.8	0.6869	.2	0.6724
65.0	0.7179	.5	0.7018	.9	0.6866	.3	0.6721
.1	0.7176	.6	0.7014	74.0	0.6863	.4	0.6718
.2	0.7172	.7	0.7011	.1	0.6859	.5	0.6715
.3	0.7168	.8	0.7007	.2	0.6856	.6	0.6711
.4	0.7165	.9	0.7004	.3	0.6853	.7	0.6708
.5	0.7161	70.0	0.7000	.4	0.6849	.8	0.6705
.6	0.7157	.1	0.6997	.5	0.6846	.9	0.6702
.7	0.7154	.2	0.6993	.6	0.6843	79.0	0.6699
.8	0.7150	.3	0.6990	.7	0.6839	.1	0.6695
.9	0.7147	.4	0.6986	.8	0.6836	.2	0.6692
66.0	0.7143	.5	0.6983	.9	0.6833	.3	0.6689
.1	0.7139	.6	0.6979	75.0	0.6829	.4	0.6686
.2	0.7136	.7	0.6976	.1	0.6826	.5	0.6683
.3	0.7132	.8	0.6972	.2	0.6823	.5	0.6679
.4	0.7128	.9	0.6969	.3	0.6819	.7	0.6676
.5	0.7125	71.0	0.6965	.4	0.6816	.8	0.6673
.6	0.7121	.1	0.6962	.5	0.6813	.9	0.6670
.7	0.7117	.2	0.6958	.6	0.6809	80.0	0.6667
.8	0.7114						

°Bé.	Sp. gr.	°Bé.	Sp. gr.	°Bé.	Sp. gr.	°Bé.	Sp. gr.
10	1.0000	7/8	0.9597	6/8	0.9226	5/8	0.8882
1/8	0.9991	16	0.9589	7/8	0.9218	6/8	0.8875
2/8	0.9982	1/8	0.9581	22	0.9211	7/8	0.8868
3/8	0.9973	2/8	0.9573	1/8	0.9203	28	0.8861
4/8	0.9964	3/8	0.9564	2/8	0.9195	1/8	0.8854
5/8	0.9956	4/8	0.9556	3/8	0.9188	2/8	0.8847
6/8	0.9947	5/8	0.9548	4/8	0.9180	3/8	0.8840
7/8	0.9938	6/8	0.9540	5/8	0.9173	4/8	0.8833
11	0.9929	7/8	0.9532	6/8	0.9165	5/8	0.8826
1/8	0.9920	17	0.9524	7/8	0.9158	6/8	0.8819
2/8	0.9912	1/8	0.9516	23	0.9150	7/8	0.8812
3/8	0.9903	2/8	0.9508	1/8	0.9143	29	0.8805
4/8	0.9894	3/8	0.9500	2/8	0.9135	1/8	0.8798
5/8	0.9885	4/8	0.9492	3/8	0.9128	2/8	0.8791
6/8	0.9877	5/8	0.9483	4/8	0.9121	3/8	0.8784
7/8	0.9868	6/8	0.9475	5/8	0.9113	4/8	0.8777
12	0.9859	7/8	0.9467	6/8	0.9106	5/8	0.8771
1/8	0.9850	18	0.9459	7/8	0.9098	6/8	0.8764
2/8	0.9842	1/8	0.9451	24	0.9091	7/8	0.8757
3/8	0.9833	2/8	0.9444	1/8	0.9084	30	0.8750
4/8	0.9825	3/8	0.9436	2/8	0.9076	1/8	0.8743
5/8	0.9816	4/8	0.9428	3/8	0.9069	2/8	0.8736
6/8	0.9807	5/8	0.9420	4/8	0.9061	3/8	0.8730
7/8	0.9799	6/8	0.9412	5/8	0.9054	4/8	0.8723
13	0.9790	7/8	0.9404	6/8	0.9047	5/8	0.8716
1/8	0.9782	19	0.9396	7/8	0.9040	6/8	0.8709
2/8	0.9773	1/8	0.9388	25	0.9032	7/8	0.8702
3/8	0.9765	2/8	0.9380	1/8	0.9025	31	0.8696
4/8	0.9756	3/8	0.9372	2/8	0.9018	1/8	0.8689
5/8	0.9748	4/8	0.9365	3/8	0.9010	2/8	0.8682
6/8	0.9739	5/8	0.9357	4/8	0.9003	3/8	0.8675
7/8	0.9731	6/8	0.9349	5/8	0.8996	4/8	0.8669
14	0.9722	7/8	0.9341	6/8	0.8989	5/8	0.8662
1/8	0.9714	20	0.9333	7/8	0.8982	6/8	0.8655
2/8	0.9706	1/8	0.9326	26	0.8974	7/8	0.8649
3/8	0.9697	2/8	0.9318	1/8	0.8967	32	0.8642
4/8	0.9689	3/8	0.9310	2/8	0.8960	1/8	0.8635
5/8	0.9680	4/8	0.9302	3/8	0.8953	2/8	0.8629
6/8	0.9672	5/8	0.9295	4/8	0.8946	3/8	0.8622
7/8	0.9664	6/8	0.9287	5/8	0.8939	4/8	0.8615
15	0.9655	7/8	0.9279	6/8	0.8931	5/8	0.8609
1/8	0.9647	21	0.9272	7/8	0.8924	6/8	0.8602
2/8	0.9639	1/8	0.9264	27	0.8917	7/8	0.8596
3/8	0.9630	2/8	0.9256	1/8	0.8910	33	0.8589
4/8	0.9622	3/8	0.9249	2/8	0.8903	1/8	0.8582
5/8	0.9614	4/8	0.9241	3/8	0.8896	2/8	0.8576
6/8	0.9605	5/8	0.9233	4/8	0.8889	3/8	0.8569

°Bé.	Sp. gr.	°Bé.	Sp. gr.	°Bé.	Sp. gr.	°Bé.	Sp. gr.
4/8	0.8563	3/8	0.8266	2/8	0.7989	1/8	0.7729
5/8	0.8556	4/8	0.8260	3/8	0.7983	2/8	0.7724
6/8	0.8550	5/8	0.8254	4/8	0.7977	3/8	0.7719
7/8	0.8543	6/8	0.8247	5/8	0.7972	4/8	0.7713
34	0.8537	7/8	0.8241	6/8	0.7966	5/8	0.7708
1/8	0.8530	40	0.8235	7/8	0.7960	6/8	0.7703
2/8	0.8525	1/8	0.8229	46	0.7955	7/8	0.7698
3/8	0.8517	2/8	0.8223	1/8	0.7949	52	0.7692
4/8	0.8511	3/8	0.8217	2/8	0.7943	1/8	0.7687
5/8	0.8504	4/8	0.8211	3/8	0.7938	2/8	0.7682
6/8	0.8498	5/8	0.8205	4/8	0.7932	3/8	9.7676
7/8	0.8491	6/8	0.8199	5/8	0.7926	4/8	0.7671
35	0.8485	7/8	0.8193	6/8	0.7921	5/8	0.7666
1/8	0.8478	41	0.8187	7/8	0.7915	6/8	0.7661
2/8	0.8472	1/8	0.8181	47	0.7910	7/8	0.7656
3/8	0.8466	2/8	0.8175	1/8	0.7904	53	0.7650
4/8	0.8459	3/8	0.8169	2/8	0.7898	1/8	0.7645
5/8	0.8453	4/8	0.8163	3/8	0.7893	2/8	0.7640
6/8	0.8446	5/8	0.8157	4/8	0.7887	3/8	0.7635
7/8	0.8440	6/8	0.8151	5/8	0.7882	4/8	0.7629
36	0.8434	7/8	0.8145	6/8	0.7876	5/8	0.7624
1/8	0.8427	42	0.8140	7/8	0.7871	6/8	0.7619
2/8	0.8421	1/8	0.8134	48	0.7865	7/8	0.7614
3/8	0.8415	2/8	0.8128	1/8	0.7860	54	0.7609
4/8	0.8408	3/8	0.8122	2/8	0.7854	1/8	0.7604
5/8	0.8402	4/8	0.8116	3/8	0.7849	2/8	0.7598
6/8	0.8396	5/8	0.8110	4/8	0.7843	3/8	0.7593
7/8	0.8390	6/8	0.8104	5/8	0.7838	4/8	0.7588
37	0.8383	7/8	0.8098	6/8	0.7832	5/8	0.7583
1/8	0.8377	43	0.8092	7/8	0.7827	6/8	0.7578
2/8	0.8371	1/8	0.8087	49	0.7821	7/8	0.7573
3/8	0.8364	2/8	0.8081	1/8	0.7816	55	0.7568
4/8	0.8358	3/8	0.8075	2/8	0.7810	1/8	0.7562
5/8	0.8352	4/8	0.8069	3/8	0.7805	2/8	0.7557
6/8	0.8346	5/8	0.8063	4/8	0.7799	3/8	0.7552
7/8	0.8340	6/8	0.8058	5/8	0.7794	4/8	0.7547
38	0.8333	7/8	0.8052	6/8	0.7789	5/8	0.7542
1/8	0.8327	44	0.8046	7/8	0.7783	6/8	0.7537
2/8	0.8321	1/8	0.8040	50	0.7778	7/8	0.7532
3/8	0.8315	2/8	0.8034	1/8	0.7772	56	0.7527
4/8	0.8309	3/8	0.8029	2/8	0.7767	1/8	0.7522
5/8	0.8302	4/8	0.8023	3/8	0.7762	2/8	0.7517
6/8	0.8296	5/8	0.8017	4/8	0.7756	3/8	0.7512
7/8	0.8290	6/8	0.8011	5/8	0.7751	4/8	0.7507
39	0.8284	7/8	0.8006	6/8	0.7746	5/8	0.7502
1/8	0.8278	45	0.8000	7/8	0.7740	6/8	0.7497
2/8	0.8272	1/8	0.7994	51	0.7735	7/8	0.7492

°Bé.	Sp. gr.	°Bé.	Sp. gr.	°Bé.	Sp. gr.	°Bé.	Sp. gr.
57	0.7487	7/8	0.7259	5/8	0.7048	3/8	0.6850
1/8	0.7482	63	0.7254	6/8	0.7044	4/8	0.6846
2/8	0.7477	1/8	0.7249	7/8	0.7040	5/8	0.6842
3/8	0.7472	2/8	0.7245	69	0.7035	6/8	0.6838
4/8	0.7467	3/8	0.7240	1/8	0.7031	7/8	0.6833
5/8	0.7462	4/8	0.7235	2/8	0.7026	75	0.6830
6/8	0.7457	5/8	0.7230	3/8	0.7022	1/8	0.6825
7/8	0.7452	6/8	0.7226	4/8	0.7018	2/8	0.6821
58	0.7447	7/8	0.7221	5/8	0.7013	3/8	0.6817
1/8	0.7442	64	0.7216	6/8	0.7009	4/8	0.6813
2/8	0.7437	1/8	0.7212	7/8	0.7004	5/8	0.6809
3/8	0.7432	2/8	0.7207	70	0.7000	6/8	0.6804
4/8	0.7427	3/8	0.7203	1/8	0.6996	7/8	0.6800
5/8	0.7422	4/8	0.7198	2/8	0.6991	76	0.6796
6/8	0.7417	5/8	0.7193	3/8	0.6987	1/8	0.6792
7/8	0.7412	6/8	0.7189	4/8	0.6983	2/8	0.6788
59	0.7407	7/8	0.7184	5/8	0.6978	3/8	0.6784
1/8	0.7403	65	0.7179	6/8	0.6974	4/8	0.6780
2/8	0.7398	1/8	0.7175	7/8	0.6970	5/8	0.6776
3/8	0.7393	2/8	0.7170	71	0.6965	6/8	0.6771
4/8	0.7388	3/8	0.7166	1/8	0.6961	7/8	0.6767
5/8	0.7383	4/8	0.7161	2/8	0.6957	77	0.6763
6/8	0.7378	5/8	0.7157	3/8	0.6952	1/8	0.6759
7/8	0.7373	6/8	0.7152	4/8	0.6948	2/8	0.6755
60	0.7368	7/8	0.7147	5/8	0.6944	3/8	0.6751
1/8	0.7364	66	0.7143	6/8	0.6939	4/8	0.6747
2/8	0.7359	1/8	0.7138	7/8	0.6935	5/8	0.6743
3/8	0.7354	2/8	0.7134	72	0.6931	6/8	0.6739
4/8	0.7349	3/8	0.7129	1/8	0.6926	7/8	0.6735
5/8	0.7344	4/8	0.7125	2/8	0.6922	78	0.6731
6/8	0.7339	5/8	0.7120	3/8	0.6918	1/8	0.6727
7/8	0.7335	6/8	0.7116	4/8	0.6914	2/8	0.6723
61	0.7330	7/8	0.7111	5/8	0.6909	3/8	0.6719
1/8	0.7325	67	0.7107	6/8	0.6905	4/8	0.6715
2/8	0.7320	1/8	0.7102	7/8	0.6901	5/8	0.6711
3/8	0.7315	2/8	0.7098	73	0.6897	6/8	0.6707
4/8	0.7311	3/8	0.7093	1/8	0.6892	7/8	0.6703
5/8	0.7306	4/8	0.7089	2/8	0.6888	79	0.6699
6/8	0.7301	5/8	0.7084	3/8	0.6884	1/8	0.6695
7/8	0.7296	6/8	0.7080	4/8	0.6880	2/8	0.6691
62	0.7292	7/8	0.7075	5/8	0.6875	3/8	0.6687
1/8	0.7287	68	0.7071	6/8	0.6871	4/8	0.6683
2/8	0.7282	1/8	0.7066	7/8	0.6867	5/8	0.6679
3/8	0.7277	2/8	0.7062	74	0.6863	6/8	0.6675
4/8	0.7273	3/8	0.7057	1/8	0.6859	7/8	0.6671
5/8	0.7268	4/8	0.7053	2/8	0.6854	80	0.6667
6/8	0.7263						

THE DETERMINATION OF ARSENIC IN GLYCERINE.

By A. C. Langmuir.

Received October 22, 1898.

THE presence of arsenic in glycerine is probably, by this time, well known to chemists. Several have described its detection qualitatively. Barton,[1] however, was the first to estimate it quantitatively. Barton's method, which was applied on C. P. glycerines only, consists in the charring of five grams of the glycerine with sulphuric and nitric acids, the production of a mirror in the Marsh apparatus, and the comparison of the mirror so obtained with a standard mirror according to Sanger's method.[2]

As it is impossible to draw an accurate comparison if the mirrors weigh over 0.06 milligram, a suitable aliquot part of the solution must be taken, in order to obtain a mirror weighing less than this amount. This requires some experimenting on the part of the analyst, which becomes very tedious if the glycerine be high in arsenic.

These considerations led the author to abandon the method and adopt a modification of Polenske's process,[3] suitable to the case at hand. The method as described by Polenske is accurate with quantities of arsenic up to four to five milligrams. As in glycerine analysis the amount of arsenic in the portion taken rarely exceeds one milligram, the apparatus may be materially simplified.

For analysis we take fifteen to twenty grams of a crude soap lye glycerine and twenty-five to thirty grams of a saponification or C. P. glycerine. With dilute glycerines an amount is taken which would yield the requisite weight upon evaporation. The weighed sample is made up to 100 cc. with hot water and rinsed into a capacious casserole, containing a mixture of 200 cc. of concentrated nitric acid and twelve cc. concentrated sulphuric acid. Cover and heat gently in the hood until the action starts. Remove the flame and wait until the violence of the reaction is over, then boil down slowly over a low flame until dense fumes of sulphuric acid appear. Raise the heat at the end to expel

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[1] This Journal..17, 883.

[2] *Proc. Am. Acad. Sci.*, *1891*, 26, 24.

[3] *Chem. Centrbl.* (*1889*), 60, [2], 58.

the last traces of nitric acid. If the concentration has been a slow one (four to five hours) the organic matter will generally be entirely oxidized. If the acid turns brown, however, from the charring of organic matter it is well to boil for some time longer to complete the oxidation. There is no danger of losing any arsenic by this treatment. Cool and dilute to fifty cc.

About forty grams of coarsely granulated zinc are placed in the generating flask of the Marsh apparatus. A 75 to 100 cc. stop-cock funnel pierces the stopper. The escaping gas is passed through a wash-bottle containing a five per cent. lead nitrate solution to remove any hydrogen sulphide and is dried by passing through a calcium chloride tube. A tube of hard glass about ten inches long and with an inside diameter of ten to twelve mm. is heated near one end and drawn out at that point to a tube with a diameter of one to one and a half mm. This section serves to catch the metallic arsenic deposited. Of the large sections the longer is heated by two Bunsen burners. To prevent sagging it is well to protect this part of the tube with a roll of copper gauze wrapped around it. The shorter section at the end of the tube holds a slip of filter-paper moistened with a saturated solution of mercuric chloride. This serves to detect the presence of any hydrogen arsenide which might pass the burners undecomposed.

After making connections ten cc. of twenty per cent. sulphuric acid is run into the flask. When the air has been entirely displaced rinse the solution to be tested into the stop-cock funnel, light the burners and run the solution, drop by drop, on the zinc at such a rate that not more than two bubbles a second pass the lead nitrate wash-bottle.

If the mercuric chloride paper should at any time show a yellowish tint the solution should be run in more slowly. If the size of the mirror shows that a considerable amount of arsenic is present, it is well to add, at the end, a little stannous chloride dissolved in hydrochloric acid. In any case add a few cubic centimeters of dilute acid after the entire solution has been run in to expel hydrogen arsenide remaining in the flask.

The section carrying the mirror is separated by a file and carefully weighed on an assay gold balance within 0.01 milligram. This can be readily done, as the weight of the tube seldom exceeds 300 milligrams. The arsenic is dissolved by dipping the tube into hot dilute nitric acid, and after washing and drying the weight is taken again, the difference being the weight of the arsenic forming the mirror. The zinc and acids used should not form a perceptible mirror after running the apparatus three quarters of an hour. The following results were obtained:

Arsenic taken. Milligrams.	Arsenic found. Milligrams.
0.20	0.17
0.50	0.45
0.75	0.68

Several C. P. glycerines were found to be free from arsenic. Arsenic was found in a majority of saponification glycerines. These averaged about 0.00018 to 0.00030 per cent. A number of crude soap-lye glycerines gave percentages lying between 0.00064 and 0.01.

A very fair idea of the arsenic contents may be gained by Gutzeit's test, using mercuric chloride instead of silver nitrate. Two cc. of glycerine are run into a five-inch test-tube and diluted with four cc. of water; a piece of granulated zinc is added and sufficient hydrochloric acid to just start the reaction. The tube is then quickly closed by a cork whose lower end is covered with a seven cm. filter-paper. The paper is wrapped around the cork so that it rests smoothly against the lower end. This part is moistened with two drops of a saturated solution of mercuric chloride. The hydrogen escapes through the creases between the paper and the tube. The evolution of hydrogen should be fairly brisk but not too violent.

After standing ten minutes the cork and paper are removed. The latter is spread out and examined. A yellow stain in the shape of a circle with a diameter equal to the end of the cork is formed if arsenic were present. With very impure glycerines the color is brown. The papers carrying the stains may be marked and kept as records for future comparisons. The color is fairly permanent. By comparing the yellow stain produced by the glycerine under examination with a series of standards prepared by running the same test on portions of a solution of arsenic (one milligram in 100 cc.), the per cent. of arsenic can be gauged quite accurately after a little practice. The color is quite distinct with 0.01 milligram of arsenic and is still perceptible with 0.0025 milligram. If the latter amount were present in two cc. glycerine (sp. gr. 1.26) the per cent. of arsenic present would be 0.00010 which would be about the limit of delicacy by this test

Gutzeit's test using silver nitrate was found to be very unsatisfactory. It is very difficult to form any idea as to the amount of arsenic present from the intensity of the color in this case. The silver nitrate is also so easily affected by impurities in the zinc and acid other than arsenic that any conclusion as to the presence of the latter should be drawn with great caution.

In view of the rapidity, delicacy, and accuracy of Gutzeit's test, using mercuric chloride, it is difficult to understand why the more laborious Marsh test should still hold its own as a qualitative test for arsenic.

LABORATORY OF RICKETTS & BANKS,
NEW YORK.

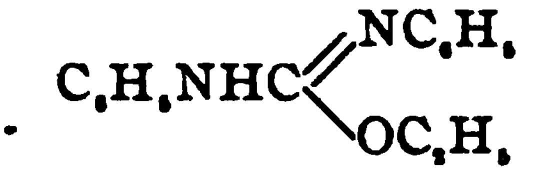
ON THE ISOUREA ETHERS AND OTHER DERIVATIVES OF UREAS.

BY F. B. DAINS.

Received December 10, 1898.

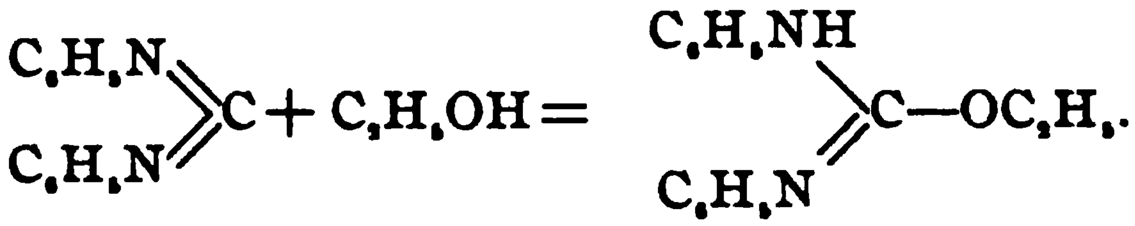
THE imido ethers, oxygen ethers of ordinary acid amides or anilides, have since their discovery by Pinner in 1883 been exhaustively investigated in many directions on account of their remarkable reactivity.

In 1894, the first representative of the oxygen ethers of a simple urea, ethyl isocarbanilide



$$C_6H_5NHC\begin{matrix}\diagup NC_6H_5\\ \diagdown OC_2H_5\end{matrix}$$

was prepared by Lengfeld and Stieglitz.[1] They found that when carbodiphenylimide was heated to 180° in a sealed tube with absolute alcohol, it added the alcohol quantitatively forming ethylisodiphenylurea.



$$\begin{matrix}C_6H_5N\diagdown\\ C_6H_5N\diagup\end{matrix}\!\!\!C + C_2H_5OH = \begin{matrix}C_6H_5NH\diagdown\\ C_6H_5N\diagup\end{matrix}\!\!\!C—OC_2H_5.$$

A little latter they discovered[2] that the ethylisodiphenylurea

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[1] *Ber. d. chem. Ges.*, 27, 926.

[2] *Am. Chem. J.*, 17, 112.

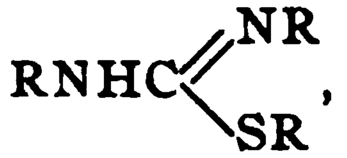
could be prepared without the use of sealed tubes by the action of sodium ethylate upon the hydrogen chloride addition-product of carbodiphenylimide

$$(C_6H_5NH)C(C_6H_5N)Cl + NaOC_2H_5 \rightarrow (C_6H_5NH)C:(NC_6H_5)OC_2H_5 + NaCl.$$

It was finally shown by Stieglitz[1] that the isocarbanilide ethers could be made in a very simple way by the action of sodium ethylate on the alcoholic solution of the carbodiphenylimide. Alcohol is taken up in the cold with great ease under these conditions, while in the absence of sodium ethylate no addition occurs at ordinary temperatures, the diimide polymerizing to $C_3(NC_6H_5)_6$.[2]

These investigations having dealt chiefly with the devising of methods for preparing isourea ethers, at the suggestion, and under the direction, of Dr. Stieglitz, the investigation of the physical constants and particularly of the chemical behavior of this new class of compounds was undertaken by me. The isourea ethers seemed unusually interesting subjects for study, since according to their constitution they are at the same time amidines and imido ethers.

Ethylisodiphenylurea has the amidine grouping, $C:(NC_6H_5)(NHC_6H_5)$, and can be called ethoxydiphenylformamidine. It also possesses the characteristic imido ether group, $C:(NC_6H_5)(OC_2H_5)$, and hence can be regarded as anilidophenylimidoformic ether. These ethers resemble also the corresponding isothiourea ethers



$$RNHC\begin{matrix}\nearrow NR\\ \searrow SR\end{matrix},$$

which are more easily prepared and which were consequently discovered,[3] and investigated earlier than the oxygen derivatives.

The most striking results that have been brought out in this investigation are less in the resemblances shown to exist between the above groups of compounds and the isourea ethers, than in the surprising discovery, how deeply the nature of the bodies is modified by the combination of the two typical amidine and imido ether groups in the same molecule.

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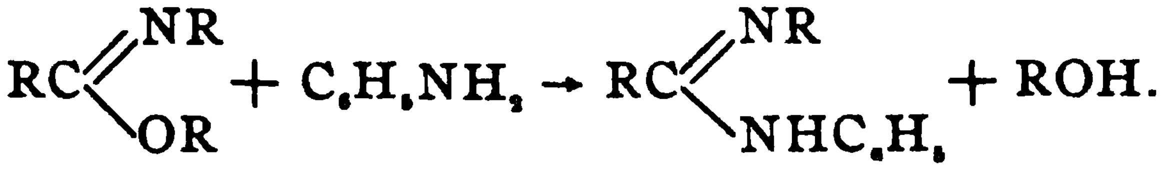
[1] *Ber. d. chem. Ges.*, 28, 573.

[2] *Ibid.*, 27, 1283; 28, 1004.

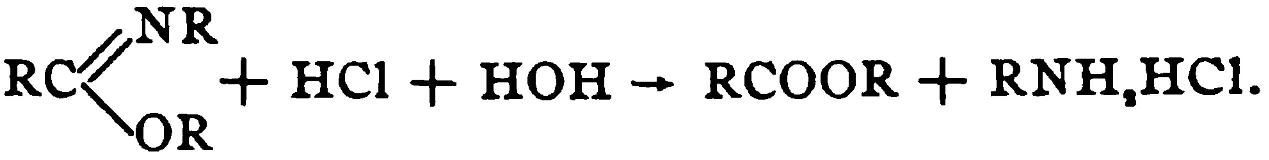
[3] *Ibid.*, 12, 1061; 14, 1490; 15, 338.

For instance the imido ethers belong to a remarkably active class of compounds,—a fact illustrated by the two following typical reactions. Aniline converts imido ethers easily and smoothly into amidines according to I.

I. 

$$\mathrm{RC}\left\langle\begin{matrix}\mathrm{NR}\\ \mathrm{OR}\end{matrix}\right. + \mathrm{C_6H_5NH_2} \rightarrow \mathrm{RC}\left\langle\begin{matrix}\mathrm{NR}\\ \mathrm{NHC_6H_5}\end{matrix}\right. + \mathrm{ROH}.$$

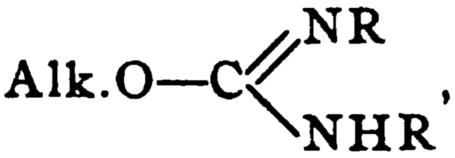
Dilute acids readily decompose the imido ethers even in the cold, forming amines and ethers as in II.

II.[1] 

$$\mathrm{RC}\left\langle\begin{matrix}\mathrm{NR}\\ \mathrm{OR}\end{matrix}\right. + \mathrm{HCl} + \mathrm{HOH} \rightarrow \mathrm{RCOOR} + \mathrm{RNH_2HCl}.$$

These investigations have proved clearly and without question, the fact that the isodialphylurea ethers give neither one of these typical reactions. The detailed description of their behavior will show that they form a new class of compounds resembling in many features the amidines, imido ethers, and isothiourea ethers, but still differing in a number of fundamental points from these classes of compounds.

Besides the study of the chemical reactions of these isoureas



$$\mathrm{Alk.O{-}C}\left\langle\begin{matrix}\mathrm{NR}\\ \mathrm{NHR}\end{matrix}\right.,$$

the methods of preparing them were tested as to their range of applicability, especially where R is an alphyl group.

Finally as a step forward in ascertaining what effect a change in the nature of R had upon the properties and reactions of the urea ethers, R was made carbethoxy ($\mathrm{—COOC_2H_5}$). Ethoxydicarbethoxyurea was prepared by a fourth method; namely, from the silver salt of dicarbethoxyurea, a method of synthesis used in the preparation of imido ethers by Tafel and Enoch,[2] Comstock and Wheeler,[3] and others, but which has hitherto failed when applied to ordinary ureas. The study[4] of these new isourea ethers has shown how profoundly a change in the nature of R modifies the chemical nature of the isoureas.

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[1] A secondary reaction sometimes occurs due to the fact that the amine formed may react with some unchanged imido ether as in I.

[2] *Ber. d. chem. Ges.*, 23, 103, 1550.

[3] *Am. Chem. J.*, 18, 1.

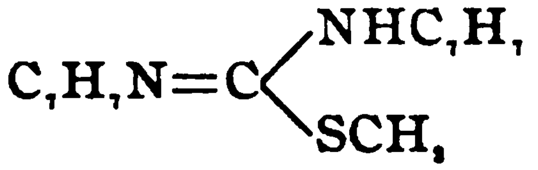
[4] The investigation of the oxygen ethers of aliphatic ureas and carbamide will be continued in this laboratory under the direction of Dr. Stieglitz.

Experimental Part.

I. PREPARATION AND PROPERTIES OF ETHERS OF ISOALPHYLUREAS.

The first ethers synthesized were derivatives of *o*-carboditolylimide, $C_7H_7N{=}C{=}NC_7H_7$.

Will and Bielschauski[1] first prepared this body by the decomposition of *o*-tolylimido-*o*-tolylthiomethylcarbamate,



$$C_7H_7N{=}C\begin{cases}NHC_7H_7\\SCH_3\end{cases}$$

This, when heated, loses mercaptan. They also obtained it by desulphurizing di-*o*-tolylthiourea with mercuric oxide in boiling benzene. It was described by them as an oil soluble in benzene and boiling over 300°.

The diimide used was prepared by this latter method, using carefully purified benzene, pure dry thiourea and yellow mercuric oxide dried at 140°. Lead oxide gives poorer results when used as a desulphurizing agent.

When freshly prepared, *o*-carboditolylimide is a pale yellow oil boiling at the following temperatures:

	Temperature.
15 mm	200°
24 mm	208
28 mm	213
34 mm	223

The index of refraction determined with an Abbe refractometer is 1.624 at the room temperature.

The diimide does not long remain an oil but soon polymerizes, becoming first sticky, then semisolid, and finally a white solid.

There are certain practical difficulties attending the preparation of the isourea ethers from the diimides, in a pure condition. The carbodiimide must be freshly prepared, since any polymerization that has occurred lessens the yield of the ether, and increases the difficulty of purification. All moisture must be carefully excluded to prevent formation of dialphylurea.

Physically these ethers are oils that must be isolated by fractionation *in vacuo* with this disadvantage; their boiling-points are high and near that of the original diimide. They are

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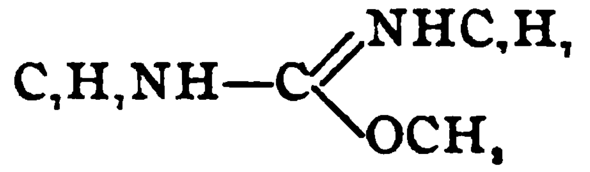
[1] *Ber. d. chem. Ges.*, 15, 1316.

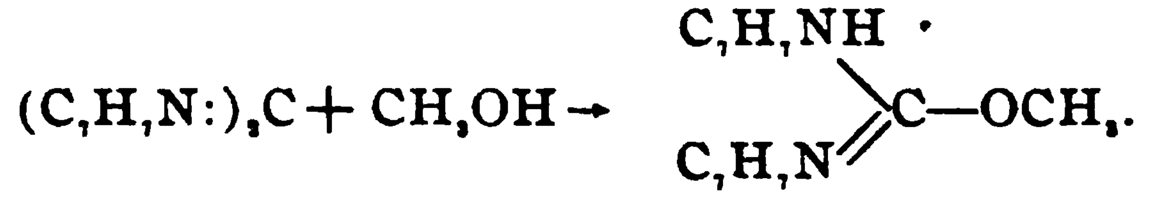
best separated from the diimide by allowing the latter to polymerize by standing, and then extracting with ligroin. This dissolves the urea ethers alone, the solid polymer being entirely insoluble in that solvent.

Methylisodi-o-tolylurea (*o-Tolylimido-o-tolylmethyl Carbamate*),



$$C_7H_7NH{-}C\begin{matrix}\nearrow NHC_7H_7\\ \searrow OCH_3\end{matrix}$$

One molecule of *o*-carboditolylimide was heated for three hours at 180°–190° with a slight excess of absolute methyl alcohol.



$$(C_7H_7N:)_2C + CH_3OH \rightarrow \begin{matrix}C_7H_7NH\\ C_7H_7N\end{matrix}\!\!>\!C{-}OCH_3.$$

The tube opened without pressure and the oily product was allowed to stand in a desiccator for three days. If unchanged carboditolylimide was present it polymerized and became insoluble in ligroin while the urea ether remained soluble. On distilling the ligroin extract, there was obtained besides traces of *o*-carbtoluide and *o*-carboditolylimide, the pure methyl ether boiling at 218° at twenty-nine mm. Analysis:

1. 0.2414 gram substance gave 0.6663 gram carbon dioxide and 0.1598 gram water.

2. 0.4514 gram substance gave 45.3 cc. moist nitrogen at 23° and 747 mm.

	Calculated for $C_{14}H_{18}N_2O$.	Found.
Carbon	75.59	75.27
Hydrogen	7.09	7.36
Nitrogen	11.02	11.17

The yield is nearly quantitative. The same ether was prepared by a second method: the action of sodium methylate in methyl alcohol solution upon the *o*-carboditolylimide. Thirty-five grams of diimide dissolved in two volumes of absolute methyl alcohol were added slowly to a solution of five grams of sodium in seventy-five cc. methyl alcohol, the whole being well cooled in a freezing mixture.

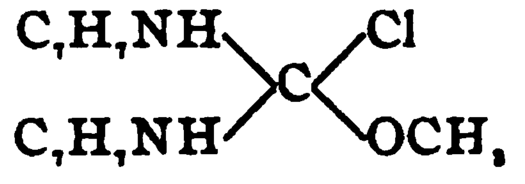
After standing over night a current of carbon dioxide was passed through it. Water was then added, the resulting oil extracted with ether, dried over sodium sulphate, and distilled. Twenty-four grams of pure methyl ether were obtained.

When freshly prepared, methylisodi-*o*-tolylurea is a colorless oil boiling at the following temperatures:

	Temperature.
11 mm	199°
18 mm	206
29 mm	218
32 mm	225

The index of refraction is 1.592 at the room temperature. In a freezing mixture the oil did not solidify but became thick and viscid. However, on standing a number of months a specimen was found to have crystallized in long blunt needles radiating from a common center. It then melted at 48.5° but otherwise exhibited all the characteristics ofthe oil. Methyliso-*o*-carbtoluide is soluble in ordinary neutral organic solvents, insoluble in water, and soluble in, and more or less rapidly decomposed by, acids such as hydrochloric and acetic.

Action of Hvdrogen Chloride (*Methylisodi-o-tolylurea Hydrochloride*,



or

$(C_7H_7NH)C : (NC_7H_7)OCH_3.HCl$.

When an ice-cold benzene solution of the methyl ether was saturated with dry hydrogen chloride, there was formed an immediate white crystalline precipitate. This was filtered off with the aid of a pump and dried on a clay plate in a vacuum desiccator over sulphuric acid, stick potash, and vaseline. Analysis:

0.1776 gram substance gave 0.0885 gram silver chloride (Carius).

	Calculated for $C_{16}H_{19}N_2OCl$.	Found.
Chlorine	12.20	12.38

Methylisodi-*o*-tolylurea hydrochloride is a white crystalline solid, insoluble in ether, benzene, and ligroin. On exposure to the air it is slowly decomposed by the moisture leaving a residue of *o*-carbtoluide. When heated with water the same decomposition is rapidly effected. In this it differs from the hydrochloride of an ordinary imido ether.

For instance benzimidoethylether hydrochloride,

$$C_6H_5C(NH)OC_2H_5,HCl,$$

is readily saponified by moisture, the products being ammonium chloride and ethyl benzoate. These reactions will be discussed later in connection with the action of aqueous acids upon the urea ethers. In the absence of moisture methyliso-*o*-carbtoluide hydrochloride is much more stable.

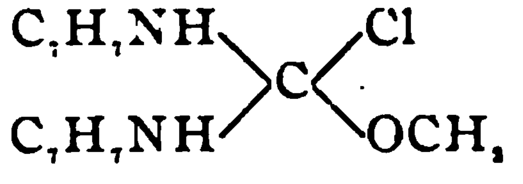
Some of the dry salt was placed in a test-tube connected with an azotometer, the whole apparatus being filled with dry carbon dioxide. At the temperature of the water-bath there was no reaction ; it required gentle heating with the free flame to cause any decomposition. Methyl chloride was then split off quantitatively and collected in the azotometer. It was identified by its burning with a green-tinged flame.

$$C_7H_7NHC : (NC_6H_5)OCH_3.HCl \rightarrow CH_3Cl + (C_7H.NH)_2CO.$$

In a stream of dry hydrogen chloride this stability is much lessened, the loss of alkyl chloride taking place then at a lower temperature. This was shown as follows: dry hydrogen chloride was passed over some of the methyl ether contained in a test-tube connected with an azotometer. At ordinary temperatures there was little decomposition, but on heating to 90° a gas was given off which was not absorbed by the caustic potash, and which burned with a green-tinged flame showing it to be methyl chloride.

The dry hydrogen chloride was first absorbed, but as the temperature increased, methyl chloride split off leaving a white residue. This, after recrystallization from benzene, had the properties and the melting-point (243°) of *o*-carbtoluide. While the hydrochlorides of imido ethers and of urea ethers react differently with moisture, the dry salts decompose with heat in an entirely analogous manner with loss of alkyl chloride.[1] For the constitution of the salts of isocarbanilidoethers, two possibilities present themselves.

I.



$$\begin{matrix} C_7H_7NH \\ C_7H_7NH \end{matrix} \Big\rangle C \Big\langle \begin{matrix} Cl \\ OCH_3 \end{matrix}$$

$$\text{II.}\quad C_7H_7NH.C(OCH_3)(NC_7H_7HCl) \text{ or}$$
$$(C_7H_7N :)C(OCH_3)(NC_7H_7H_2Cl).$$

This question will be discussed later. One fact will be

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[1] Pinner : *Ber. d. chem. Ges.*, 16, 1654.

brought out here, and that is that although the isocarbanilido ethers are anilidoimido ethers, they are monoacid bases uniting with but one equivalent of hydrogen chloride even in the presence of a large excess of the acid.

This is fully confirmed by the composition of the two chlorplatinates of isocarbanilido ethers which I prepared: those of methyliso-*o*-carbtoluide and of ethylisocarbanilide.

Chlorplatinate of Methyl Iso-o-carbtoluide,

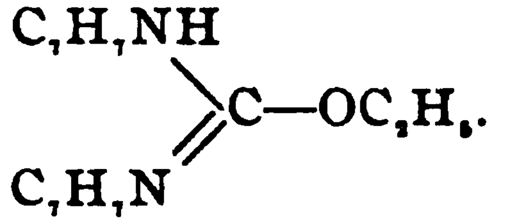
$$[(C_7H_7NH)C(:NC_7H_7)OCH_3]_2H_2PtCl_6.$$

When absolute alcohol solutions of the methyl ether and of chlorplatinic acid were mixed and allowed to stand in a desiccator, the chlorplatinate slowly separated out. It formed hard, red crystals which melted at 155° with decomposition. Analysis:

0.1366 gram substance gave 0.0290 gram platinum.

	Calculated for $C_{32}H_{38}N_4O_2PtCl_6$.	Found.
Platinum	21.25	21.23

Ethylisodi-o-tolylurea (*o-Tolylimido-o-tolyl Ethylcarbamate*),



$$\begin{matrix}C_7H_7NH \\ \quad\rangle C—OC_2H_5. \\ C_7H_7N\end{matrix}$$

One molecule of *o*-carboditolylimide was heated with a slight excess of absolute ethyl alcohol at 180°–190° for three hours. The oily contents of the tube were fractionated and a pure product boiling at 215.5° at twenty-four mm. obtained. Analysis:

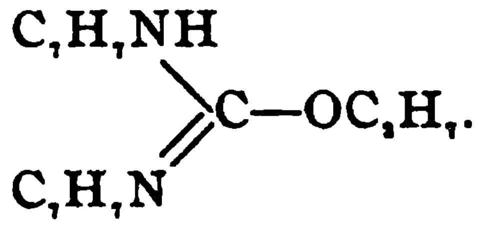
0.2177 gram substance gave 21.55 cc. moist nitrogen at 25° and 745 mm.

	Calculated for $C_{17}H_{20}N_2O$.	Found.
Nitrogen	10.45	10.80

Ethylisodi-*o*-tolylurea is a colorless oil which does not solidify at —5°. Its index of refraction is 1.606 at the room temperature. Heated to 80° in a stream of dry hydrogen chloride, ethyl chloride is split off, leaving a solid residue of *o*-carbtoluide. This was recrystallized from benzene and identified by its properties and melting-point.

In the preparation of urea ethers by the method given too high temperatures must be avoided. This was shown in the following experiment. A mixture of diimide and absolute alcohol was heated at 215°–220° for several hours and then for a short time at 250°. The tube opened with much pressure and a gas escaped that burned with a luminous flame. This was probably ethylene. The contents of the tube consisted of an oil and a white solid which proved to be *o*-carbtoluide. The oil yielded on distillation *o*-ditolylurea, *o*-carboditolylimide and only a small amount of impure ethylisocarbtoluide. This was identified by the formation of ethyl chloride which burned with a green-tinged flame. As will be seen later the above substances are the decomposition products of the ethyl ether at high temperatures.

n-Propylisodi-o-tolylurea,



Twenty grams of the carbodiimide and ten grams propyl alcohol were heated at 180°–200° for six hours. The tube opened without pressure and the oil on distillation gave the pure propyl ether. The yield is nearly quantitative. Analysis:

0.4246 gram substance gave 39.5 cc. moist nitrogen at 22° and 744 mm. pressure.

	Calculated for $C_{18}H_{22}N_2O$.	Found.
Nitrogen	9.93	10.36

n-Propylisodi-*o*-tolylurea is a colorless oil, soluble in ordinary organic solvents. It does not solidify in a freezing-mixture. The boiling-point is 212°–214° at fourteen mm.

Dry hydrogen chloride was passed into a solution of the propyl ether in benzene and ligroin. The slight white precipitate first formed readily dissolved as the current of gas was continued. An oil which was soluble in benzene but insoluble in ligroin separated out on standing. This, when heated, gave propyl chloride and *o*-carbtoluide, showing that it contained the hydrochloride. An effort was made to isolate this as follows:

The oil obtained by the action of hydrogen chloride was washed with a mixture of benzene and ligroin (b. p. 40°–60°), and the excess of solvent evaporated in a current of dry air in a vacuum desiccator over stick potash, sulphuric acid, and vaseline. A clear, yellow oil resulted. Analysis:

0.5610 gram substance heated with lime required 15.8 cc. tenth-normal silver nitrate (Volhard).

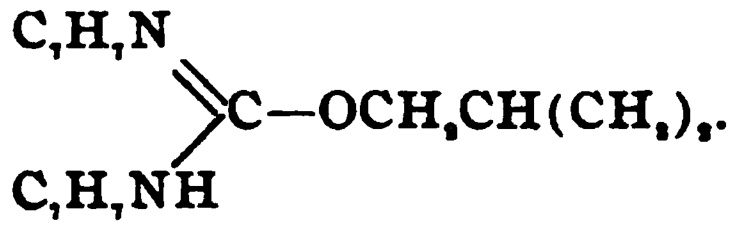
0.5166 gram substance gave 32.8 cc. moist nitrogen at 17.5° and 740 mm.

	Calculated for $C_{18}H_{23}N_2OCl$.	Found.
Chlorine	11.13	9.98
Nitrogen	8.79	7.18

The low results are doubtless due to traces of solvent obstinately retained by the oil. That it is mainly the hydrochloride is shown by the analysis and the decomposition products, propyl chloride and *o*-carbtoluide.

The oil solidified on standing in a desiccator but, as analysis indicated, this was caused by the gradual formation of *o*-ditolylurea.

Isobutylisodi-o-tolylurea,



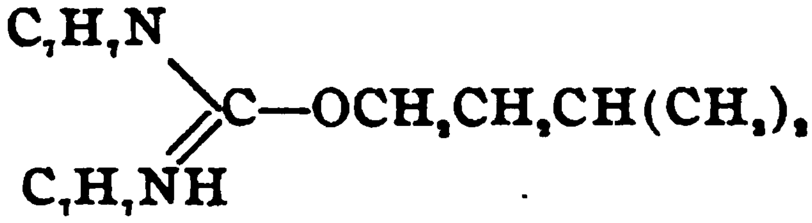
$$\begin{matrix} C_7H_7N \\ C_7H_7NH \end{matrix} > C{-}OCH_2CH(CH_3)_2.$$

Sixteen grams of *o*-carboditolylimide were heated for six hours at 180°–210° with a slight excess of isobutyl alcohol. The contents of the tube yielded on distillation a clear colorless oil, boiling at 218° at 18 mm. Analysis showed that it was the isobutyl ether.

0.3250 gram substance gave 27.7 cc. moist nitrogen at 24° and 755 mm.

	Calculated for $C_{19}H_{24}N_2O$.	Found.
Nitrogen	9.46	9.54

Isoamylisodi-o-tolylurea,



$$\begin{matrix} C_7H_7N \\ C_7H_7NH \end{matrix} > C{-}OCH_2CH_2CH(CH_3)_2.$$

Forty-one grams diimide were dissolved in amyl alcohol (b. p. 130°–131°), and then poured into a well-cooled solution of sodium amylate (one molecule). The mixture became slightly warm. After standing over night carbon dioxide was passed into the solution, which was then washed with water, dried with sodium sulphate, and distilled. The pure amyl ether was obtained as a colorless oil boiling at 206° at 10 mm. Its index of refraction is 1.572 at the room temperature. The yield is about equal to the diimide taken. Analysis:

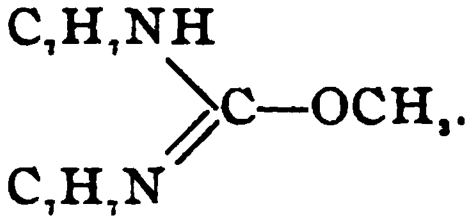
0.3586 gram substance gave 29.2 cc. moist nitrogen at 18° and 747 mm.

	Calculated for $C_{20}H_{26}N_2O$.	Found.
Nitrogen	9.03	9.28

p-Carboditolylimide, $C_7H_7N{=}C{=}NC_7H_7$.—This was prepared in the hope that the higher melting para-derivatives would give solid ethers instead of oils—a wish that was not realized. The diimide was first described by Will[1] as a body melting above 60° and boiling above 300° without decomposition. The substance was made in the usual manner by the desulphurization of the thiourea. In general *p*-carboditolylimide is less reactive than the carbodiphenyl or *o*-ditolylimides. The para body and its ethers distil about 20° higher than the corresponding *o*-tolyl compounds and tend to form viscid gums difficult to purify.

Pure *p*-carboditolylimide is a pale yellow oil boiling at 221°–223° at 20 mm.

Methyl Isodi-p-tolylurea,



$$\begin{matrix} C_7H_7NH \diagdown \\ \qquad\qquad C{-}OCH_3. \\ C_7H_7N \diagup\!\!\diagup \end{matrix}$$

Twenty-three grams of the diimide were heated with methyl alcohol for seven hours at 180°–200°. In distilling the product a considerable portion came over below 200°. From the higher fraction, there was isolated the pure methyl ether boiling at 220° at fifteen mm. Analysis:

0.4580 gram substance gave 43.8 cc. moist nitrogen at 16° and 739 mm.

	Calculated for $C_{16}H_{18}N_2O$.	Found.
Nitrogen	11.02	10.89

The methyl ether forms a clear, thick oil. In a stream of dry hydrogen chloride it is somewhat more stable than the methyl iso-*o*-carbtoluide, since methyl chloride only splits off above 100°. From the fraction below 200° an oil was obtained which boiled at 86°–88° at fourteen mm. and which turned red on standing. This gave the following results on analysis:

0.4148 gram substance gave 0.3202 gram water and 1.1510 grams carbon dioxide.

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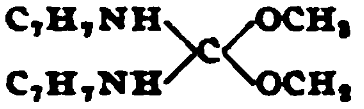
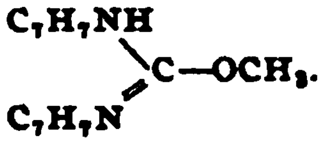
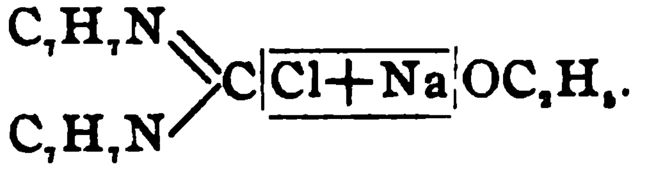
[1] *Ber. d. chem. Ges.*, 14, 1488.

0.3108 gram substance gave 27.5 cc. moist nitrogen at 16.5° and 736 mm.

	Calculated for  $(C_7H_7NH)_2C(OCH_3)_2$	 $C_7H_7NH(C_7H_7N{=})C{-}OCH_3$.	Found.
Carbon	71.33	75.70	75.59
Hydrogen	7.69	8.58	8.66
Nitrogen	9.79	11.02	10.24

It was thought that the compound might be the dimethyl ether, but the theory was not borne out by the analytical figures. At the same time, while the results agree fairly closely with those required for an isomeric ether, the great difference in boiling-point, 140° at fourteen mm., would seem to preclude this idea. Owing to lack of material, further examination of this oil was deferred for the present.

Methyl isodi-*p*-tolylurea was also prepared by another method, the action of sodium methylate on the monohydrochloride of *p*-carboditolylimide.



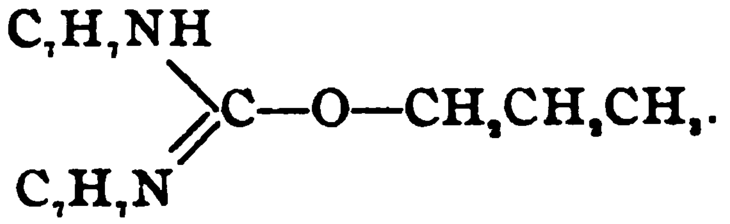
$$(C_7H_7N{=})(C_7H_7N{-})C\boxed{Cl+Na}OC_2H_5.$$

One molecule of hydrogen chloride in ether solution was added to *p*-carboditolylimide also dissolved in ether. No effort was made to isolate the hydrochloride, but sodium methylate in methyl alcohol was added directly to the solution. After filtering off the sodium chloride and some *p*-carbtoluide, the ether was evaporated and the residue extracted with ligroin. This, on distillation, gave a poor yield of methyl isodi-*p*-tolylurea.

0.4488 gram substance gave 46 cc. moist nitrogen at 25° and 755 mm.

	Calculated for $C_{16}H_{18}N_2O$.	Found.
Nitrogen	10.02	11.42

n-Propyl Isodi-p-tolylurea,



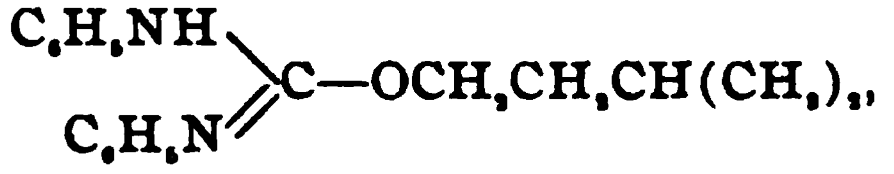
$$C_7H_7NH(C_7H_7N{=})C{-}O{-}CH_2CH_2CH_3.$$

On heating propyl alcohol and *p*-carboditolylimide at 180° for four hours, the propyl ether which boils at 221° at sixteen mm. was formed. It is a thick viscid oil at ordinary temperatures. Analysis:

0.4380 gram substance gave 36.8 cc. moist nitrogen at 18° and 760 mm.

	Calculated for $C_{18}H_{22}N_2O$.	Found.
Nitrogen	9.93	9.75

Isoamylisodiphenylurea,



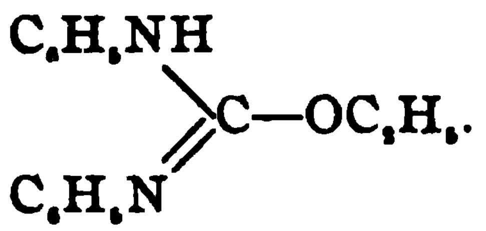
$$\begin{array}{l} C_6H_5NH \diagdown \\ \qquad\qquad\;\; C—OCH_2CH_2CH(CH_3)_2, \\ C_6H_5N \diagup\!\!\diagup \end{array}$$

was prepared by the action of sodium amylate upon carbodiphenylimide in amyl alcohol (b. p. 130°–131°) solution. The procedure was the same as with the isoamyliso-*o*-carbtoluide. It is a colorless oil boiling at 210° at fifteen mm. At the room temperature the index of refraction is 1.594. Analysis:

0.2280 gram substance gave 19.5 cc. moist nitrogen at 16° and 749 mm.

	Calculated for $C_{18}H_{22}N_2O$.	Found.
Nitrogen	9.93	9.86

Ethylisocarbanilide,



$$\begin{array}{l} C_6H_5NH \\ \qquad\quad \rangle C—OC_2H_5. \\ C_6H_5N \end{array}$$

This was prepared by Lengfeld and Stieglitz,[1] who described it as a limpid stable oil boiling at 200° at 20 mm. They also isolated the hydrochloride of the ethyl ether, a white solid melting at 60°–80° with decomposition. Its action toward chlorplatinic acid is interesting.

It has been shown previously that methyl isodi-*o*-tolylurea with chlorplatinic acid, gives in absolute alcohol solution, an anhydrous salt in which the urea ether acts as a monacid base. On the other hand ethyl isocarbanilide forms, in absolute alcohol solution, no crystallizable derivative of the ethyl ether, but, in dilute alcoholic solutions, gives very readily a chlorplatinate containing water of crystallization. To a water solution of chlorplatinic acid was added a dilute alcoholic solution of ethyl isocarbanilide. On evaporation, the platinum salt separated out in the form of hard, red crystals which melted at 113° with decomposition. Analysis:

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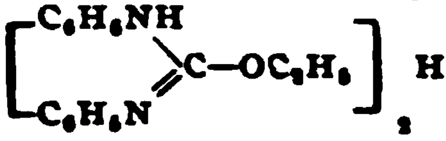
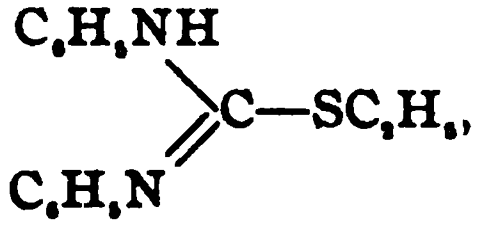
[1] *Ber. d. chem. Ges.*, 27, 926.

I. 0.1630 gram substance gave 0.0330 gram platinum.
II. 0.3750 gram substance gave 0.0762 gram platinum.

	Calculated for  $H_2PtCl_6 + 4H_2O$.	Found. I.	II.
Platinum	20.28	20.25	20.32

The same salt is formed in both dilute and concentrated alcoholic solutions. The corresponding thioether,



gives a platinum salt containing two molecules of water of crystallization.[1] In the preparation of the urea ethers described above, three methods have been used.

1. The addition of alcohol at high temperatures to the carbodiimide.
2. The action of sodium ethylate upon an alcoholic solution of the carbodiimide.
3. The action of sodium ethylate upon the monochloride of the carbodiimide.

Of these methods, the first gives good results and is of universal applicability. It requires, however, the use of sealed tubes. The second method gives equally good yields; it does not require high temperatures, and by it larger amounts of the urea ether can be prepared at one time. It necessitates, however, the use of a large excess of the alcohol. The third method offers no advantage over the other two. It involves the intermediate formation of the monohydrochloride, a compound very sensitive toward moisture. It requires also a greater number of operations with a corresponding decrease in yield.

The urea ethers thus far prepared are, with one exception, oils; methyl iso-*o*-carbtoluide alone on long standing solidified to a crystalline mass. On the other hand ethyl isocarbanilide, prepared in 1894 by Dr. Stieglitz, is still an unchanged oil.

The urea ethers dissolve readily in neutral organic solvents and are insoluble in water. All acid solvents react with them. While they cannot be distilled at ordinary pressure without

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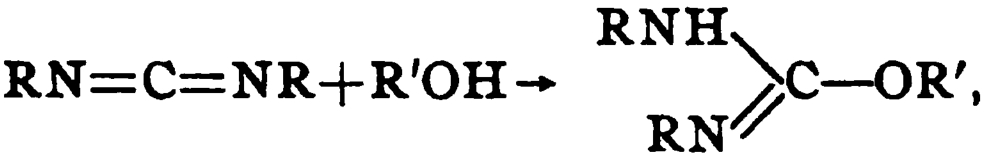
[1] Rathke: *Ber. d. chem. Ges.*, 14, 1776..

decomposition, they can uniformly be fractionated *in vacuo* without change. The index of refraction is in all cases observed less than that of the original diimide. This can serve as a test of the purity of the ether since the presence of the diimide causes an increase in the index of refraction.

INDEX OF REFRACTION.

Carbodi-*o*-tolylimide	1.624
Methyl iso-*o*-carbtoluide	1.692
Ethyl iso-*o*-carbtoluide	1.606
Amyl iso-*o*-carbtoluide	1.572
Ethyl isocarbanilide[1]	1.6028
Amyl isocarbanilide	1.594

The experiments just described show that the formation of a urea ether by the addition of an alcohol to the carbodiimide is a general reaction of which all aromatic carbodiimides are capable; these take up the various primary and secondary fatty alcohols without difficulty. In every case the alcohol was added smoothly according to

I. 

$$RN{=}C{=}NR + R'OH \rightarrow \begin{matrix} RNH \\ RN \end{matrix}\!\!>\!C{-}OR',$$

and with none of the many alcohols tested did the carbodiimide simply cause the splitting off of water according to

$$\text{II. } (RN{:})_2C + C_nH_{2n+1}OH \rightarrow (RNH)_2CO + C_nH_{2n},$$

forming a carbanilide and an unsaturated hydrocarbon.

Such compounds were indeed obtained by heating carbodi-*o*-tolylimide and ethyl alcohol much higher than the temperatures necessary for forming the urea ethers,[2] but, as will be shown later, the urea ethers themselves give, on heating the same products, a carbanilide and an olefine hydrocarbon.

$$\text{III. } RNHC({:}NC)OC_nH_{2n+1} \rightarrow (RNH)_2CO + C_nH_{2n}.$$

These facts prove that either urea ethers are formed as intermediate products when carbodiphenylimide and an alcohol react according to II, or that the absorption of alcohol by the unsaturated carbodiphenylimide molecule to form a urea ether takes

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[1] J. Stieglitz: *Ber. d. chem. Ges.*, 28, 574.

[2] Page 143.

place much below the temperature at which an alcohol breaks down into water and an olefine.

$$\text{IV. } C_nH_{2n+1}OH \rightleftarrows C_nH_{2n} + H_2O.$$

Such a reaction would become one-sided from the absorption of water by the carbodiphenylimide according to

$$\text{V. } H_2O + C(:NC_6H_5)_2 \rightarrow (C_6H_5NH)_2CO,$$

and give the reaction products of II.

Either of these conclusions—and there is no other third possible view of the action of carbodiphenylimide on the alcohols—is sufficient to throw clear light on some of the next reactions that were studied, and in the interpretation of the results of such study reference will be made to the conclusions just established.

II. ISOACYLALPHYLUREAS; ACTION OF DRY ACIDS ON CARBODIIMIDES.

The ease with which carbodiphenylimide absorbs alcohols suggested the attempt to prepare by the same kind of reaction,—using acids—a most interesting group of bodies, the acid salts of carbodiphenylimide or isoacylcarbanilides according to

$$\text{VI. } (C_6H_5N:)_2C + HOAcyl \rightarrow (C_6H_5NH)C(:NC_6H_5)OAcyl.$$

As such salt like isoacyl derivatives the addition products of carbodiphenylimide and hydrogen chloride must be considered, and these were investigated by me somewhat further than they had been previously. Weith,[1] by passing dry hydrogen chloride into a benzene solution of carbodiphenylimide, prepared the monochloride which he analyzed and to which he assigned the formula $(C_6H_5N)_2C.HCl$.

Further investigation by Lengfeld and Stieglitz[2] showed the conditions for preparing the monochloride, and proved that a dichloride $(C_6H_5N)_2 2HCl$ and a sesquichloride $[(C_6H_5N)_2C]_2 3HCl$ are much more readily precipitated even if much less than one molecular equivalent of hydrogen chloride is used. These are white crystalline compounds that can be isolated and analyzed. Such salts were also obtained by me from the carboditolylimides and carboallylphenylimide.

Work done in this laboratory by Mr. H. N. McCoy,[3] under the

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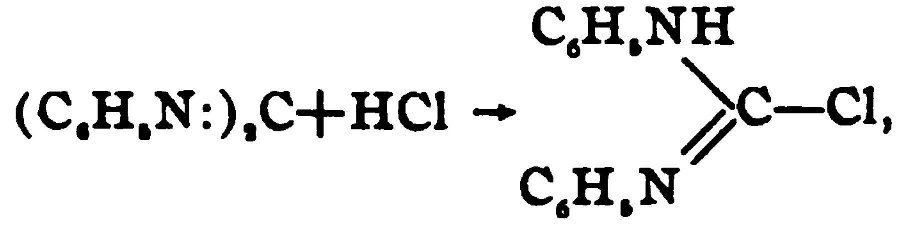
[1] *Ber. d. chem. Ges.*, 7, 11.

[2] *Am. Chem. J.*, 17, 107.

[3] *Ibid.*, 21, 111; *Ber. d. chem. Ges.*, 30, 1090, 1685.

direction of Professor Stieglitz, has fully confirmed the conclusions of Stieglitz and Lengfeld that the monochloride has the constitution of an isoacylcarbanilide



$$(C_6H_5N{:})_2C + HCl \rightarrow \begin{matrix} C_6H_5NH \\ C_6H_5N \end{matrix}\!\!>\!C{-}Cl,$$

and still it has the appearance of a salt.[1] I have been able to confirm the salt-like character of such a monochloride[2]—whatever its constitution—by preparing chlorplatinates of analogous composition, which in appearance, composition, and behavior resemble the chlorplatinates of any organic base.

Action of Hydrochloric Acid and of Hydrochlorplatinic Acid on the Carbodialphylimides; Monochlorplatinate of Carbodiphenylimide, $[(C_6H_5N)_2C]_2H_2PtCl_6$.—When an absolute alcohol solution of carbodiphenylimide is treated with chlorplatinic acid also dissolved in absolute alcohol, a darkening in color occurs, but there is no precipitate unless the solution is very concentrated. In that case a dark, red salt separates. This melts at 155°–165° and contains, as shown by analysis, an excess of platinum over that required by the monochlorplatinate. (26.00 per cent. instead of 24.44). If ether be added to the clear alcoholic solution, a yellow platinum salt corresponding to the monochlorplatinate is obtained. This was washed with ether, dried at 90°, and analyzed. Analysis:

0.1118 gram substance gave 0.0270 gram platinum.

	Calculated for $[(C_6H_5N{:})_2]_2H_2PtCl_6$.	Found.
Platinum	24.44	24.15

The chlorplatinate[3] is soluble in alcohol, insoluble in ether, and not readily decomposed by water. It begins to decompose at 143° and melts completely to a reddish oil at 150°. In several cases a salt containing one or two per cent. more of platinum with a higher melting-point (155°–165°) was obtained, but in no instance did this correspond to the dichlorplatinate,

$$[(C_6H_5N)_2C].H_2PtCl_6(Pt=32.19).$$

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[1] The dichloride must therefore have the constitution $(C_6H_5NH)_2CCl_2$ or $Cl.C(C_6H_5NH){:}(C_6H_5N)HCl$. The former is more likely and is being further investigated in this laboratory.

[2] *Am. Chem. J.*, 21, 101.

[3] It can also be prepared by mixing ethereal solutions of the diimide and chlorplatinic acid. It is then precipitated out immediately.

The Dichlorplatinate of Carbodiphenylimide, $[(C_6H_5N:)_2C]$-H_2PtCl_6.—The latter body, the chlorplatinate, corresponding to the dichloride, was not formed by the action of an excess of chlorplatinic acid upon the diimide. This was in decided contrast to the action of hydrogen chloride upon the diimide. Thus carbodiphenylimide monochloride was isolated with considerable difficulty by Lengfeld and Stieglitz,[1] who prepared it by passing hydrogen chloride into a solution of the carbodiimide; but there was a constant tendency for the reaction to go farther and form the sesqui- and dichlorides.

The dichlorplatinate of carbodiphenylimide was, however, obtained in the following unexpected manner: An effort was made to prepare an anhydrous chlorplatinate of ethyl isocarbanilide using absolute alcohol solutions; with dilute alcohol a hydrated salt is obtained.[2] While this end was not realized a still more interesting compound, the platinum salt of carbodiphenylimide dichloride was obtained.

When absolute alcoholic solutions of ethyl isodiphenyl urea and chlorplatinic acid were mixed, there gradually separated out, in small quantity, reddish-brown needles which did not melt at 250°. For analysis these crystals were washed with alcohol and ether and dried at 80°. Analysis:

I. 0.0802 gram substance gave 0.0258 gram platinum.

II. 0.1325 gram substance gave 0.0430 gram platinum.

	Calculated for $[(C_6H_5N)_2C]H_2PtCl_6$.	Found. I.	Found. II.
Platinum	32.30	32.17	32.45

The results agree with the composition of the platinum salt of carbodiphenylimide dichloride. So far as the analysis is concerned it agrees also with the composition of aniline chlorplatinate (Pt=32.80), but against this latter view are the following facts:

a. The salt does not resemble at all in appearance aniline chlorplatinate.

b. The salt after treatment with caustic soda did not respond to the bleaching-powder test for aniline.

c. Aniline could only be formed from urea ether hydrochloride by saponification as follows:

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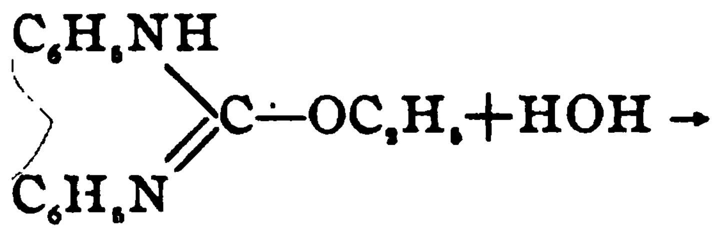
[1] *Am. Chem. J.*, 17, 110.

[2] Page 148.



$C_6H_5NH_2.HCl + C_6H_5NHCOOC_2H_5$.

The residue was examined but no trace of phenyl urethane could be detected.

Such a chlorplatinate of carbodiphenylimide could, however, be formed as follows:

In the absolute alcohol solution slight dissociation might occur into alcohol and carbodiphenylimide. This latter then unites with the chlorplatinic acid which was present in very great excess, forming the dichlorplantinuate of carbodiphenylimide.

o-Carboditolylimide Dichloride, $C_7H_7N:C(NHC_7H_7)Cl.HCl$.—It had been previously noted by Will and Bielschauski[1] that a solution of *o*-carboditolylimide with hydrogen chloride gave a white precipitate, but the product formed was not analyzed. Dry hydrochloric acid gas was passed into *o*-carboditolylimide dissolved in twenty times its weight of dry benzene.

The diimide must be especially purified by several distillations, otherwise gummy impurities are found. The stream of gas was continued as long as any absorption took place, the solution meanwhile being kept cool. A heavy white precipitate formed at first which soon redissolved, and on standing there was deposited from the clear solution hard granular crystals. These were dried on a clay plate in a vacuum desiccator over sulphuric acid, stick potash, and vaseline for thirty-six hours. Analysis:

0.1898 gram heated with lime required 13.37 cc. tenth-normal silver nitrate (Volhard).

	Calculated for $C_{15}H_{16}N_2Cl_2$.	Found.
Chlorine	24.06	24.96

o-Carboditolylimide is a white solid, insoluble in ligroin and benzene, but soluble in chloroform. It melts with decomposition at 235°–237°. Moisture decomposes it giving *o*-carbtoluide and hydrogen chloride.

$$(C_7H_7NH)C : (NC_7H_7)Cl.HCl + H_2O \rightarrow 2HCl + (C_7H_7NH)_2CO.$$

o-Carboditolylimide Monochlorplatinate, $[(C_7H_7N)_2C]_2H_2PtCl_6$.—Ethereal solutions of the diimide and of chlorplatinic acid were

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[1] *Ber. d. chem. Ges.*, 15, 1316.

mixed; a yellow platinum salt was immediately precipitated which was washed with ether dried at 100°, and analyzed. Analysis:

0.1850 gram substance gave 0.0420 gram platinum.

	Calculated for $[(C_7H_7N)_2C]_2H_2PtCl_6$.	Found.
Platinum	22.84	22.70

The salt begins to decompose at 146°-148°; at about 155° it melts completely. The same salt was obtained even with a large excess of chlorplatinic acid.

p-Carboditolylimide Monochlorplatinate.—This body which was prepared from ethereal solutions of chlorplatinic acid and *p*-carboditolylimide as in the previous cases, is a yellow salt that begins to decompose at 148° and melts completely between 155° and 160°.

0.1828 gram substance gave 0.0410 gram platinum. Analysis:

	Calculated for $[(C_7H_7N)_2C]H_2PtCl_6$.	Found.
Platinum	22.84	22.43

Sesquichloride of p-Carboditolylimide.—When a concentrated benzene solution of pure-*p*-carboditolylimide was saturated with dry hydrochloric acid gas, the solution which became warm was filled with a thick, heavy, white precipitate of the hydrochloride. Analysis showed that this was a mixture of chlorides and not a definite chemical compound.

Two determinations of different preparations gave respectively 17.80 and 17.33 per cent. chlorine. The monochloride contains 13.73 per cent. chlorine, the sesquichloride 19.21 per cent., and the dichloride 24.06 per cent.

With a five per cent. benzene solution better results were obtained. The precipitate first formed nearly all dissolved on continuing the stream of gas, while the filtered solution on standing a few hours in a vacuum desiccator deposited a large crop of crystals. These melted at 126°-127° forming an oily gum. Analysis:

I. 0.2418 gram substance heated with lime required 13.1 cc. tenth-normal silver nitrate (Volhard).

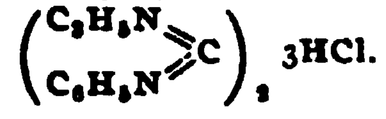
II. 0.1840 gram substance required 10.1 cc. tenth-normal silver nitrate.

	Calculated for $(C_{15}H_{14}N_2)_2 3HCl$.	Found. I.	Found. II.
Chlorine	19.22	19.20	19.46

Sesquichloride of Carboallylphenylimide.—Analogous results were obtained with carboallylphenylimide. The experiments with hydrogen chloride will be given here, but the discussion of the diimide reserved until later.

Dry hydrochloric acid gas was passed into a benzene solution of carboallylphenylimide. A precipitate formed, which, as the current of gas was continued, almost entirely dissolved. The filtered solution, on standing, deposited crystals. These were dried on a clay plate in a vacuum desiccator over sulphuric acid, stick potash, and vaseline, and analyzed. Analysis:

0.1778 gram substance heated with lime required 12.23 cc. tenth-normal silver nitrate.



$$\left(\begin{matrix} C_3H_5N \\ C_6H_5N \end{matrix} \!\!> C\right)_2 3HCl.$$

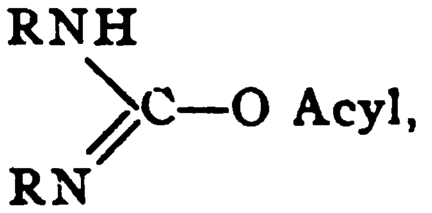
	Calculated for $\left(\begin{matrix} C_3H_5N \\ C_6H_5N \end{matrix} \!\!> C\right)_2 3HCl$.	Found.
Chlorine	25.00	24.39

The monochloride requires 18.23 per cent. chlorine and the dichloride 30.73 per cent. The product obtained is evidently a sesquichloride. Lengfeld and Stieglitz,[1] who first prepared a body of this class—carbodiphenylimide sesquichloride, say this regarding it: "The substance may be a mixture of monochloride and dichloride in nearly molecular quantities. It was very frequently obtained and seems to have more or less characteristic properties by which it can be identified."

But the fact that three different carbodiimides give compounds of this class argues strongly in favor of a definite chemical composition and against their being merely mechanical mixtures.

These sesquichlorides, $[(RN:)_2C]. 3HCl$, show an interesting analogy to the isocyanides which also form hydrochlorides of this type, $(RNC)_2 3HCl$.[2]

The Action of Organic Acids upon the Carbodialphylimides, as has been stated previously, was studied with the object of obtaining isoacylureas of the general type



$$\begin{matrix} RNH \\ RN \end{matrix} \!\!> C—O\ Acyl,$$

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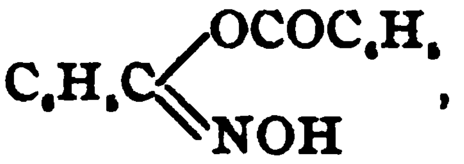
[1] *Am. Chem. J.*, 17, 110.

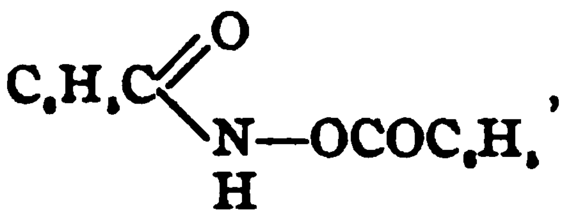
[2] Gautier: *Ann. chim. phys.*, 17, 223; Nef: *Ann. Chem.* (Liebig), 270, 277; *Ber. d. chem Ges.*, 31, 1770.

corresponding to the alkyl ethers and the chlorides just described. This seemed an especially inviting subject for investigation since the instances of true isoacyl derivatives of acid amides are exceedingly rare, and their behavior very interesting. Such an acyl derivative was prepared by Werner[1] in the form of dibenzhydroximic acid,



$$C_6H_5C\begin{matrix}\diagup OCOC_6H_5\\ \diagdown NOH\end{matrix},$$

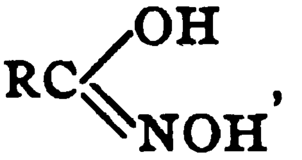
by the action of silver benzoate on benzhydroximic acid chloride. He found it a peculiarly reactive body since, even on standing, it suffers molecular change going over into its isomer,



$$C_6H_5C\begin{matrix}\diagup\!\!\!\diagup O\\ \diagdown \underset{H}{N}\text{—}OCOC_6H_5\end{matrix},$$

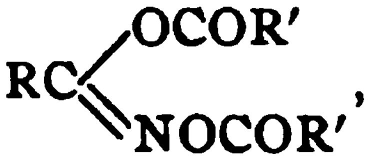
the benzoyl ester of benzhydroxamic acid.

If both hydrogen atoms of a hydroxamic acid,



$$RC\begin{matrix}\diagup OH\\ \diagdown\!\!\!\diagdown NOH\end{matrix},$$

are replaced by acyl groups,



$$RC\begin{matrix}\diagup OCOR'\\ \diagdown\!\!\!\diagdown NOCOR'\end{matrix},$$

such molecular change is prevented and more stable bodies are obtained. These, however, with alkali lose with great ease the acyl group joined to carbon.[2] These facts would indicate the reactivity and unstability of the acyl isomers, could they be isolated.

The organic acids, such as acetic and formic, do react very readily with the carbodiimides even at low temperatures, and although the desired acyl isoureas were not isolated, a very interesting reaction was discovered, in which there is hardly any doubt that the acyl isoureas figure as intermediate products.

Ten grams of *o*-carboditolylimide were treated with an excess

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[1] *Ber. d. chem. Ges.*, 27, 2198.

[2] Jones: *Am. Chem. J.*, 20, 19 and 32.

of glacial acetic acid. The mixture became decidedly warm and soon solidified, while a distinct odor of acetic anhydride manifested itself.

The solid residue, after purification with ligroin and benzene, was dried on a clay plate. Its properties, melting-point (243°), and analysis showed that it was *o*-carbtoluide.

Analysis:

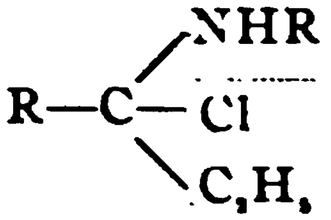
0.2418 gram substance gave 25.2 cc. moist nitrogen at 20° and 747 mm.

	Calculated for $C_{15}H_{16}N_2O$.	Found.
Nitrogen	11.66	11.77

In a second experiment ten grams of *o*-carboditolylimide (one mol.) were mixed with five grams of glacial acetic acid (two molecules) in a distilling bulb. When the reaction was completed and the product distilled from an air-bath, the main portion of the distillate came over between 130°-138°. It was fairly constant at 137°. This liquid had the odor and boiling-point of acetic anhydride and reacted directly with aniline, giving acetanilide. The residue in the flask proved to be *o*-carbtoluide.

The low temperature at which the reaction occurs is shown by the following experiment: A ligroin solution of acetic acid was added slowly to a ligroin solution of the diimide cooled to —18°. At —15° the formation of *o*-carbtoluide was very slow; at 0° the reaction went somewhat faster and at ordinary temperatures was soon over.

In view (1) of the facts discussed previously[1] that alcohols are added to the carbodiimides much below the temperature at which they suffer loss of water; (2) the very ready formation, isolation, and analysis of the dichlorides of carbodiphenylimide and *o*-carboditolylimide; (3) the decomposition of hydrochlorides of imido ethers according to



$$R-C\begin{cases}NHR\\Cl\\C_2H_5\end{cases}$$

into acid amides and alkyl chlorides, a decomposition that

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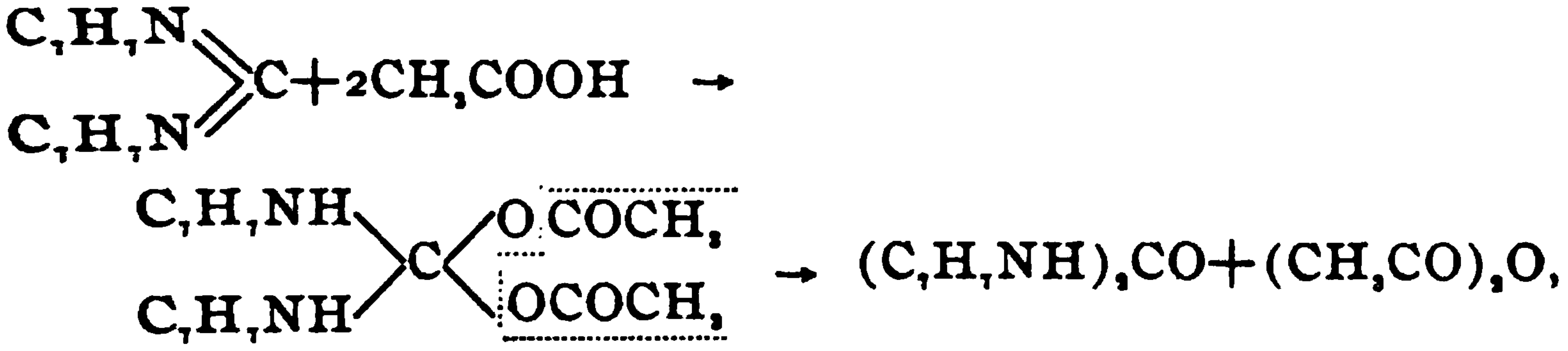
[1] Page 150.

takes place the more readily the more acid the molecule;[1] (4) the fact that the reaction takes place at —10°, a temperature at which glacial acetic acid does not lose water nor carbodiimide take it up, the formation of acetic anhydride by the action of acetic acid upon *o*-carboditolylimide cannot possibly be considered as due to direct splitting off of water from the acid. The facts mentioned show rather that the results must be due to a series of reactions; as with hydrogen chloride, there must be addition of the acetic acid to the double bond of the *o*-carboditolylimide forming a very unstable diacetate, which even at temperatures below zero decomposes, forming acetic anhydride and *o*-carbtoluide,



$$\begin{matrix} C_7H_7N \\ C_7H_7N \end{matrix} \!\!>\! C + 2CH_3COOH \rightarrow \begin{matrix} C_7H_7NH \\ C_7H_7NH \end{matrix} \!\!>\! C \!<\!\! \begin{matrix} OCOCH_3 \\ OCOCH_3 \end{matrix} \rightarrow (C_7H_7NH)_2CO + (CH_3CO)_2O,$$

corresponding to the loss of an alkyl chloride and the formation of an acid amide above.[2]

Action of Formic Acid.—Since this reaction, at so low a temperature(—15°) resulted in the formation of an acid anhydride, it was tried with formic acid whose anhydride $(CHO)_2O$ is as yet unknown.

Again, it was found that instead of such an anhydride carbon monoxide was formed.[3] *o*-Carboditolylimide diluted with an equal volume of benzene, was put in a test-tube fitted with a small dropping-funnel and connected with an azotometer. The air in the apparatus was displaced with dry carbon dioxide and the diimide solution cooled to —10°.

Pure formic acid was allowed to flow into the diimide slowly, when a gradual evolution of gas, unabsorbed by the caustic potash, occurred. On removing the freezing-mixture the evolution

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[1] Thus the chloride of ethylphenylimidochlorformate, $Cl—C(:MR)OC_2H_5$, decomposes at —15° (Lengfeld and Stieglitz, *Am. Chem. J.*, 16, 73) and the hydrochloride of ethoxydicarbethoxyurea,

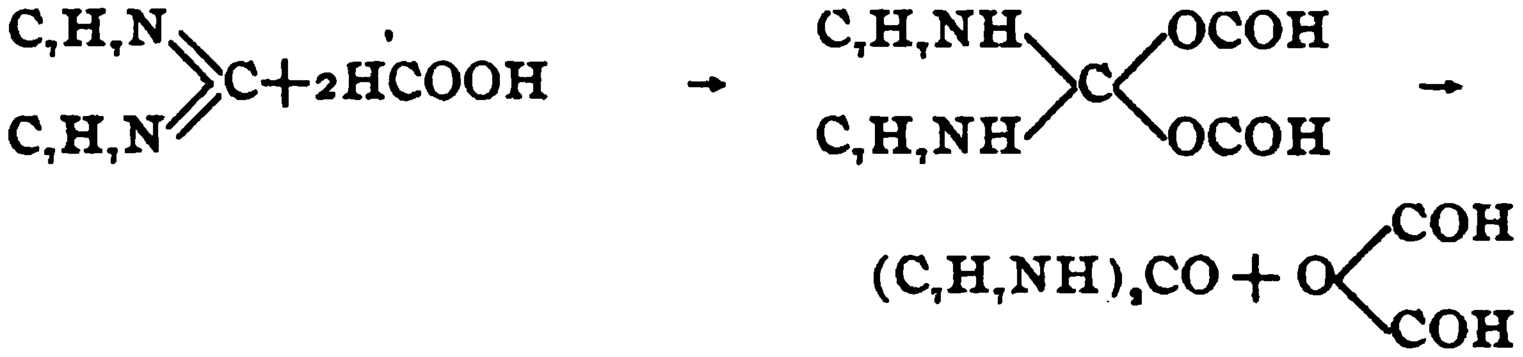
$$\begin{matrix} C(OC_2H_5)NHCOOR \\ \| \\ NCOOR \end{matrix}$$

loses ethyl chloride at 0° (page 188).

[2] Page 158.

[3] Nef: *Ann. Chem.* (Liebig), 270, 278.

of gas became more rapid and the benzene solution was filled with a white precipitate. This was found to be *o*-carbtoluide while the gas in the azotometer burned with a blue flame and proved to be carbon monoxide. As with the acetate, there must be formation of a diformate which, even at —15°, separates into *o*-carbtoluide and formic anhydride. This latter compound, which has never been isolated, breaks down immediately into carbon monoxide and water.



$$\begin{matrix} C_7H_7N \\ C_7H_7N \end{matrix} \!\!> C + 2HCOOH \rightarrow \begin{matrix} C_7H_7NH \\ C_7H_7NH \end{matrix} \!\!> C < \!\! \begin{matrix} OCOH \\ OCOH \end{matrix} \rightarrow$$

$$(C_7H_7NH)_2CO + O < \!\! \begin{matrix} COH \\ COH \end{matrix}$$

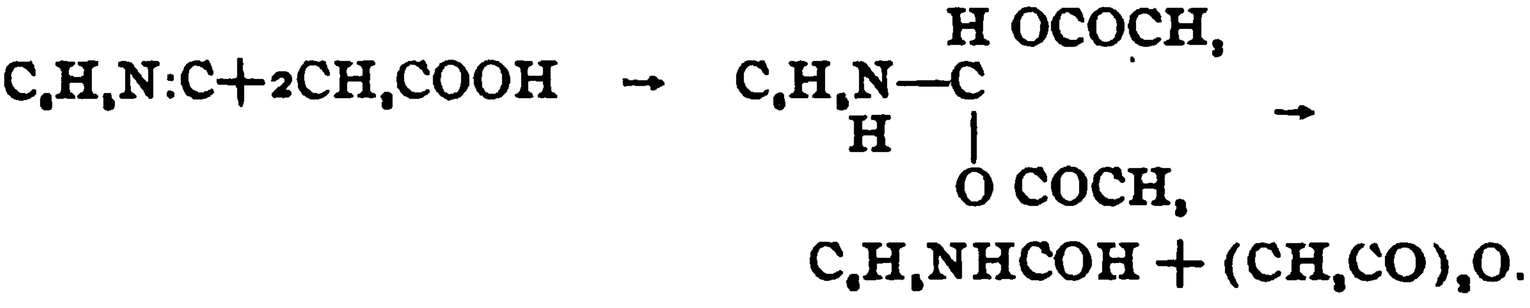
$$(COH)_2O \rightarrow 2CO + H_2O.$$

The grouping $RN{=}C{=}$ is common to both the carbodiimides, $RN{=}C{=}NR$, and the isonitrils, $RN{=}C{=}$, and the experiments just given bring out two interesting analogies between them.

These are (1) the formation of sesquichlorides, $(RNC)_2 3HCl$, and (2) the formation of acid anhydrides with acetic and formic acids.

Gautier,[1] in his researches upon the isonitrils, discovered that methyl and ethyl isocyanide give with acetic acid the anhydride.

Nef[2] more recently has shown that phenyl isocyanide reacts in like manner with acetic and formic acids at —10° giving the acid anhydride or carbon monoxide and formanilide. The facts enumerated above show that the result in these cases is also probably due to a like sequence of reactions.



$$C_6H_5N{:}C + 2CH_3COOH \rightarrow C_6H_5\underset{H}{N}{-}\overset{H\ OCOCH_3}{\underset{O\ COCH_3}{C}} \rightarrow$$

$$C_6H_5NHCOH + (CH_3CO)_2O.$$

One molecule of acid adds to the bivalent carbon; the other to the double bond between carbon and nitrogen.

Since the isoacyl derivatives were found to be so unstable

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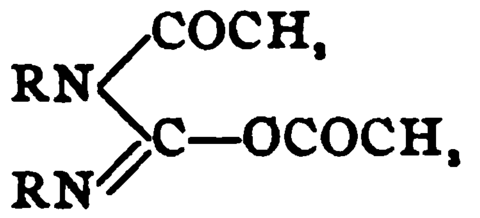
[1] Gautier: *Ann. chim. phys.*, [4], 17, 223, 241.

[2] Nef: *Ann. Chem.* (Liebig), 270, 277, 278.

splitting off acid anhydrides even at —10°, the action of acetic anhydride upon the diimide was tried as it was possible that an acetyl isoacetate like



would be more stable. Molecular proportions of acetic anhydride and *o*-carboditolylimide were mixed. Since no reaction occurred at ordinary temperature, the mixture was then heated at 160° for several hours in a sealed tube. The tube opened with much pressure due to carbon dioxide. The product of the reaction was an oil which did not solidify on standing.

It was doubtless more or less pure *o*-diacettoluide, which is itself an oil. No effort was made to isolate it but it was treated directly with dilute caustic soda and the resulting *o*-acettoluide purified and identified.

$$\text{I. } (RN{:})_2C + 2(CH_3CO)_2O \rightarrow CO_2 + 2RN(COCH_3)_2.$$

$$\text{II. } RN(COCH_3)_2 + NaOH \rightarrow CH_3COONa + RNHCOCH_3.$$

It is possible that addition-products are formed analogous to those mentioned before but they are hardly of sufficient importance to be discussed here.

III. CARBOALLYLPHENYLIMIDE.

Only one attempt has as yet been made to prepare an isourea ether of an aliphatic amine. For this purpose carboallylphenylimide was chosen. This seemed especially suitable, since, according to Bizio,[1] allylphenylthiourea gives a carbodiimide, and the ethers of such a body containing both an aliphatic and an alphyl group should show a gradation in properties between the fatty and aromatic isourea ethers.

While the efforts to obtain the isourea ethers in a pure condition were unsuccessful in this case, the results of the experiments shed interesting light upon carboallylphenylimide and correct some errors that have crept into the literature of the allylphenyl derivatives. Zinin[2] first tried the desulphurization of allylphenylthiourea. He used lead oxyhydrate in alcoholic

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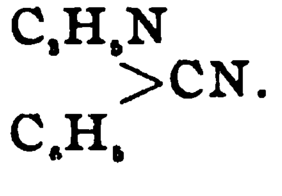
[1] Bizio : *Jsb. d. Chem.*, *1861*, 497.

[2] Zinin : *Ibid.*, *1862*, 628.

solution and obtained a compound which was described as crystallizing in long silky needles; no melting-point was given.

Bizio[1] repeated this work and isolated a body which melted at 105°. To this he ascribed the formula $C_{10}H_{10}N_2$ and the constitution



$$\begin{matrix} C_3H_5N \\ & >CN. \\ C_6H_5 \end{matrix}$$

In Beilstein's "Handbuch" and in Watts' "Dictionary of Chemistry" this same compound is called phenylallylcyanamide or carboallylphenylimide and to it is given the normal carbodiimide constitution,

$$C_6H_5N{=}C{=}NC_3H_5.$$

That this compound is carboallylphenylimide is impossible both from its method of preparation and its properties.

The thiourea was desulphurized in dilute alcohol solution and the resulting product was soluble in acetic acid without change; both reactions should give an oxygen urea and this was found to be no exception to the rule. The allylphenylthiourea was desulphurized in the usual manner with mercuric oxide in absolute benzene solution. After evaporating off the benzene a mobile oil was left, but on distillation it gave no pure products. At ten mm. pressure fractions were collected between (I) 150°–165°; (II) 165°–170°; (III) 190°–200°. This latter is the boiling-point of carbodiphenylimide.

Fraction I was analyzed and gave figures agreeing with carboallylphenylimide.

Analysis:

0.2502 gram substance gave 38.5 cc. moist nitrogen at 18° and 749 mm.

	Calculated for $C_{10}H_{10}N_2$.	Found.
Nitrogen	17.72	17.58

It, however, is not quite pure, since whenever any attempt was made to redistil it, some decomposition occurred with the formation of a high boiling residue.

In the hope that the corresponding urea ethers might be more stable, the undistilled carboallylphenylimide was treated in abso-

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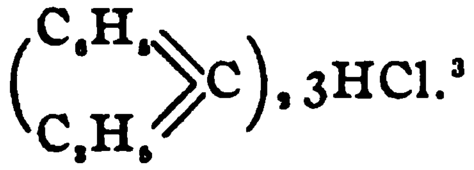
[1] *Jsb. d. Chem*, *1861*, 497; *J. prakt. Chem.*, 86, 292.

lute alcohol solution with sodium ethylate. The urea ether was isolated in the usual manner.

When the urea ether was distilled fractions were obtained that gave ethyl chloride with hydrochloric acid showing the presence of a urea ether, but no compound of a definite boiling-point could be obtained. These results indicated the impossibility of obtaining a pure carbodiimide or urea ether by distillation; hence the attempt in this direction was abandoned.

The mobile oil just described as being obtained when allylphenylthiourea ether is desulphurized with mercuric oxide in benzene solution, is very different in appearance and properties from the carboallylphenylimide described in literature as a solid (m. p. 105°) and obtained by desulphurization in dilute alcohol solution. It seemed now of interest to ascertain whether the undistilled oil is the carbodiimide and also to find out what Bizio's product that melted at 105° really was. Any analytical determinations of the composition of this oil would be of little value since it cannot be obtained entirely pure, but that it is nearly pure carboallylphenylimide is proved by its reactions and the products derived from them.

As has been shown[1] distillation breaks it up into mixtures of carboallylphenylimide, carbodiallylimide, and carbodiphenylimide. It reacts, like other carbodiimides, with alcohol and sodium alcoholate giving impure urea ethers.[2] With dry hydrogen chloride it forms a definite sesquichloride,



$$\left(\begin{matrix} C_6H_5 \\ C_3H_5 \end{matrix}\!\!>\!C\right)_2 3HCl.^3$$

It has just been shown[4] that the carbodiimides react smoothly with formic acid with the evolution of carbon monoxide and the formation of the corresponding urea.

The oily diimide was treated with formic acid. Abundant evolution of a gas occurred; this burned with a blue flame and proved to be carbon monoxide. The residue was purified by crystallization from water. A small amount of diphenylurea melting at 235° was obtained, but the main product was a solid

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[1] Page 162.

[2] Page 162.

[3] Page 156.

[4] Page 159.

melting at 113°. Later experiments showed that this solid was pure allylphenylurea formed according to

$$C_6H_5N:C:NC_3H_5+2HCOOH \rightarrow \begin{matrix}C_6H_5NH\\ C_3H_5NH\end{matrix}\!>CO+2CO+H_2O.$$

These reactions, together with its method of preparation, conclusively show that the oil really is a carbodiimide, and its almost quantitative conversion into allylphenylurea proves that, undistilled, it is nearly pure carboallylphenylimide.[1]

Bizio prepared his so-called carboallylphenylimide melting at 105° by desulphurizing the thiourea in alcoholic solution. This work was repeated to see if like results could be obtained. The semisolid product of the reaction was purified by crystallization from dilute alcohol and hot water. In one experiment a small quantity of diphenylurea was isolated, but the main product is the same solid, melting at 113°, that was obtained by the interaction of formic acid on carboallylphenylimide, and which, as will presently be shown, is allylphenylurea. The change in melting-point from 105° to 113° is due to a complete purification of the compound.

Allylphenylurea, $C_6H_5NHCONHC_3H_5$.—As the melting-point 113° does not correspond to the melting-points given in literature, either for allylphenylurea, 97°, nor for diallylurea,[2] 100°, these two ureas were prepared synthetically. Diallylurea, which was made by the desulphurization of allyl mustard oil in alcoholic solution differs widely in appearance and properties (m. p. 100°) from the above body (m. p. 113°). Allylphenyl-

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[1] An effort was made to ascertain the composition of this oil by changing it into a guanidin derivative. Equal molecules of aniline and allylphenylthiourea were boiled with mercuric oxide in dilute alcoholic solution. This should give allyldiphenyl guanidine. The gummy mass left after distilling off the alcohol was repeatedly extracted with boiling dilute hydrochloric acid and the hydrochloride obtained subjected to fractional crystallization. The fractions all gave the same base, which was curiously enough triphenyl guanidine. This was proved by its melting-point, 148°, and the analysis of the platinum salt.

I. 0.5217 gram substance gave 0.1032 gram platinum.

II. 0.2700 gram substance gave 0.0525 gram platinum.

	Calculated for $C_{38}H_{36}N_6PtCl_6$.	Found. I.	II.
Platinum	19.82	19.78	19.44

No other definite compound could be isolated.

[2] Maly: *Z.* (2), 5, 258.

[3] Will: *Ann. Chem.* (Liebig), 52, 25.

urea was made from allylamine and phenyl isocyanate.[1] The method suggested by Gabriel and Eschenbach[2] was found to give good results in the preparation of allylamine.

Ethereal solutions of allylamine and phenyl isocyanate reacted readily with the formation of an oil which, after treatment with water, solidified. The allylphenylurea was purified by crystallization from the same solvent. It then formed fine needles, melting at 113°, soluble in hot water and ordinary organic solvents.

Analysis:

0.2060 gram substance gave 29 cc. moist nitrogen at 24° and 753 mm.

	Calculated for $\left.\begin{matrix}C_6H_5NH\\C_3H_5NH\end{matrix}\right>CO.$	Found.
Nitrogen	15.91	15.73

This synthetic allylphenylurea is identical in appearance, properties, and melting-point with the compounds obtained by desulphurizing allylphenylthiourea in alcoholic solution, and by treating carboallylphenylimide with formic acid. Mixtures of these with the synthetic preparation melted constantly at 113°, thus proving their identity.

The compound prepared by Bizio[3] and described in literature as carboallylphenylimide is therefore not that, but the corresponding urea; and the melting-point of pure allylphenylurea is 113°, and not 97° as given by Maly.[4]

CHEMICAL BEHAVIOR OF THE ISOUREA ETHERS.

Besides the experiments upon the preparation of alphyl and acyl isourea ethers and of isoallylphenylureas, attention was paid particularly to a thorough investigation of the action of

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[1] The phenyl isocyanate was prepared as follows: A mixture of five grams phenyl urethane and six grams phosphorus pentachloride was heated at 70° in a distilling-bulb fitted with an air-condenser until no further evolution of gas took place. The phosphorus oxychloride was then distilled over, at the temperature of the water-bath, in a current of dry hydrogen chloride. After driving off the excess of hydrochloric acid gas with a stream of dry air, the residue was distilled. The yield of phenyl isocyanate was nearly quantitative, and the reaction seems to be a most convenient one for rapidly preparing small quantities of phenyl isocyanate. This method is one suggested by Lengfeld and Stieglitz (*Am. Chem. J.*, 15, 71) and later used by Folin for preparing isocyanates (*Am. Chem. J.*, 19, 336).

[2] *Ber. d. chem. Ges.*, 30, 1124.

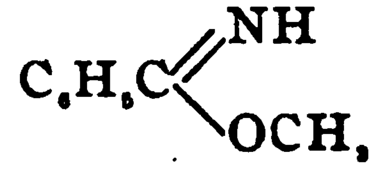
[3] *Jsb. d. Chem.*, *1861*, 497.

[4] *Z.* (2), 5, 258.

various reagents upon the isourea ethers, especially reagents that are typical in their action upon the amidines, imido ethers, and thio urea ethers.

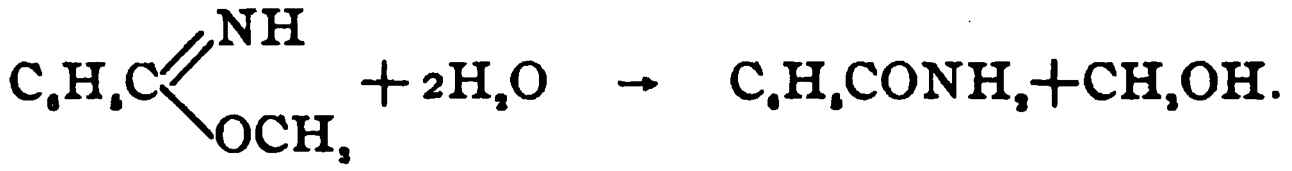
Action of Water.—Ethyl isodiphenylurea is insoluble in water and can remain in contact with it for long periods without formation of carbanilide, or other noticeable change.

No decomposition followed when a mixture of the ether with a large excess of water was evaporated almost to dryness. This is in marked contrast to the imido ethers. Thus benzimidomethyl ether,[1]



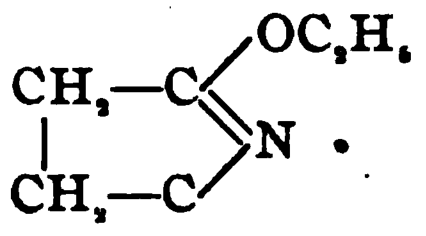
$$C_6H_5C\begin{cases}NH\\OCH_3\end{cases}$$

on exposure to the air or in water solution, after a month's standing, changes to benzamide.



$$C_6H_5C\begin{cases}NH\\OCH_3\end{cases} + 2H_2O \rightarrow C_6H_5CONH_2 + CH_3OH.$$

Comstock and Wheeler[2] have also shown that oxygen ethyl succinimide,



with water regenerates succinimide with great ease, while traces of moisture entirely prevent its preparation.

The Action of Dilute Hydrochloric Acid.—It has been shown in an earlier part of this paper that the isourea ethers unite easily and smoothly with dry hydrogen chloride to form definite crystalline hydrochlorides, which in the absence of moisture, are stable at ordinary temperatures. When heated, the dry salts split quantitatively into alkyl chloride and dialphyl urea. In the main, the same general reaction was found to occur in aqueous solutions. Methyl isodi-*o*-tolylurea was dissolved in very dilute hydrochloric acid with the aid of a few drops of alcohol, and the solution allowed to stand at the ordinary temperature. In a few hours crystals began to appear which gradually increased in amount, until the solution was examined a month later.

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[1] Wheeler: *Am. Chem. J.*, 17, 398.

[2] *Ibid.* 13, 7.

The crystalline deposit proved to be *o*-carbtoluide (m. p. 243°).[1] The clear solution, on warming with a few drops of hydrochloric acid, gave a slight precipitate of *o*-carbtoluide, showing that a little unchanged ether was still present after remaining a month in the acid solution. When the latter solution was made alkaline with ammonia a slight white deposit was obtained, which corresponded to the properties and melting-point of tri-*o*-tolylguanidine.

Ethylisodiphenylurea was dissolved in one per cent. hydrochloric acid under like conditions. A slow deposition of carbanilide began, which was not complete after a month's standing. On warming the solution still more carbanilide was thrown down, showing that the solution still contained unchanged urea ether. The clear filtrate gave, with ammonium hydroxide, only traces of triphenylguanidine (m. p. 143°). At 100° this same decomposition is fully completed in a few hours. Methylisodi-*o*-tolylurea was heated for four hours with dilute hydrochloric acid in a Victor Meyer water-bath. The tube opened with slight pressure, due to methyl chloride which burned with a green flame. The other products were, as before, *o*-ditolylurea, and traces of tritolylguanidine. The action of hydrogen chloride in aqueous solution upon ethyl isocarbanilide yields, therefore, carbanilide and ethyl chloride, according to

$$RNH.C(NR)OC_2H_5+HCl \rightarrow RNHCONHR+C_2H_5Cl.$$

Many experiments were made in the effort to trace out the course of this exceedingly important reaction so that it could be positively ascertained whether the reaction followed the lines of the decomposition of ordinary imido ethers, and if it did not, to ascertain wherein the difference lay.

When phenylbenzimidoethyl ether is allowed to stand in hydrochloric acid solution,[2] or is warmed with the same, the reaction which occurs proceeds in two stages: There is first, saponification into aniline hydrochloride and ethyl benzoate; secondly, the aniline hydrochloride reacts with unchanged imido ether to form diphenylbenzamidine and alcohol.

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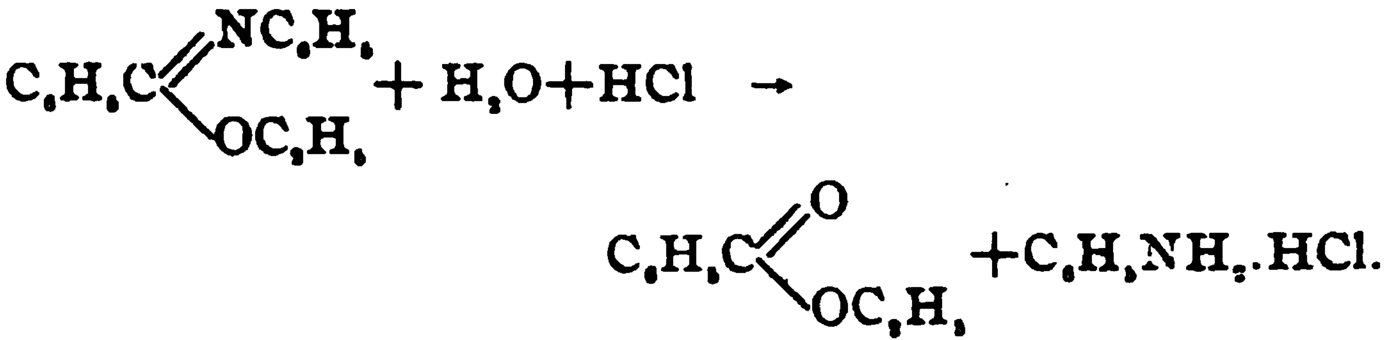
[1] The identity of these compounds was proved by taking the melting-point of a mixture of the suspected body with one of known constitution.

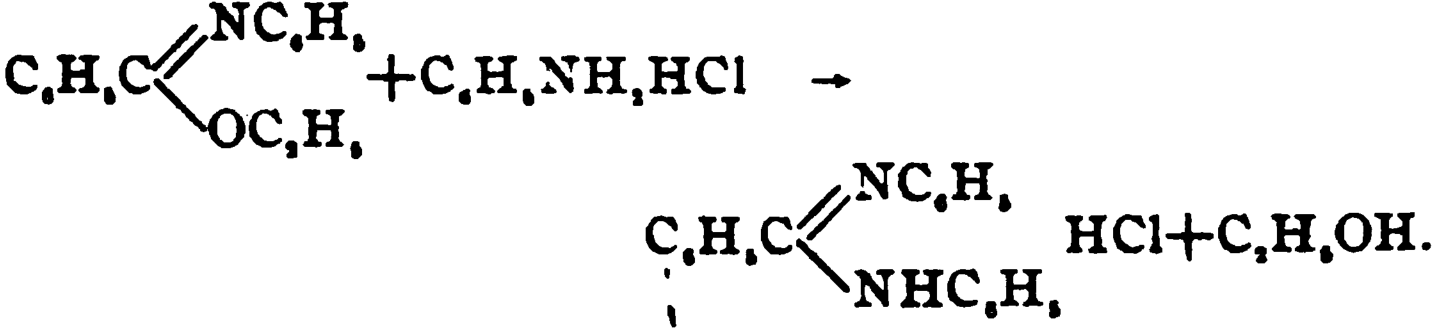
[2] *Ann. Chem.* (Liebig), 265, 138.

I.



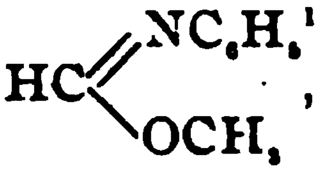
$$C_6H_5C{\genfrac{}{}{0pt}{}{\diagup NC_6H_5}{\diagdown OC_2H_5}} + H_2O + HCl \rightarrow C_6H_5C{\genfrac{}{}{0pt}{}{\diagup O}{\diagdown OC_2H_5}} + C_6H_5NH_2.HCl.$$

II.



$$C_6H_5C{\genfrac{}{}{0pt}{}{\diagup NC_6H_5}{\diagdown OC_2H_5}} + C_6H_5NH_2HCl \rightarrow C_6H_5C{\genfrac{}{}{0pt}{}{\diagup NC_6H_5}{\diagdown NHC_6H_5}} HCl + C_2H_5OH.$$

Toward dilute acid, or even water alone, methyl isoformanilide,

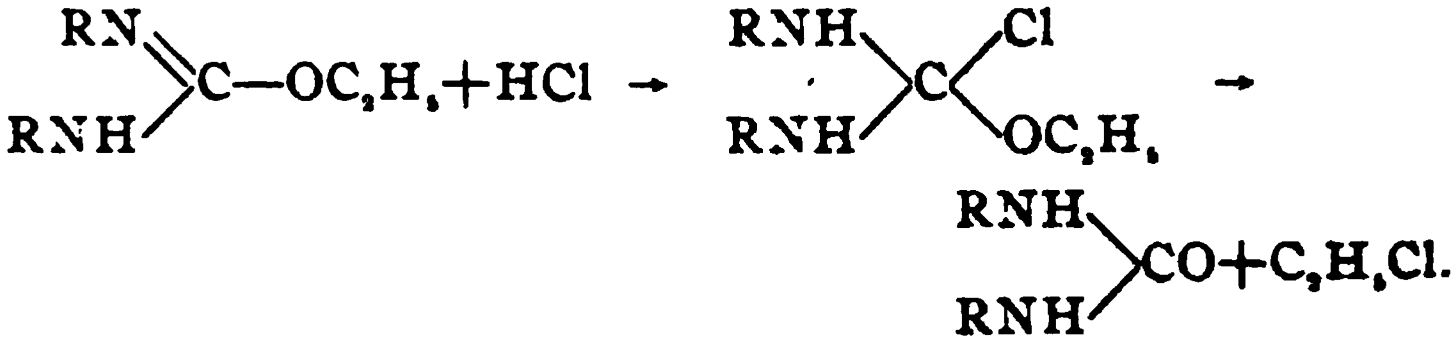


$$HC{\genfrac{}{}{0pt}{}{\diagup NC_6H_5}{\diagdown OCH_3}}\text{[1]},$$

is peculiarly sensitive. The first products are methyl formate and aniline hydrochloride, but this latter immediately reacts with unchanged imido ether to give much diphenylformamidine. The primary products, then, of the decomposition of ordinary imido ethers, are esters and amine hydrochlorides, while a secondary reaction yields amidine hydrochlorides and alcohol. No ethyl chloride is formed in dilute aqueous solution.

When the isourea ethers are decomposed in aqueous solution into ethyl chloride and carbanilide, several possibilities present themselves for the mechanism of the reaction.

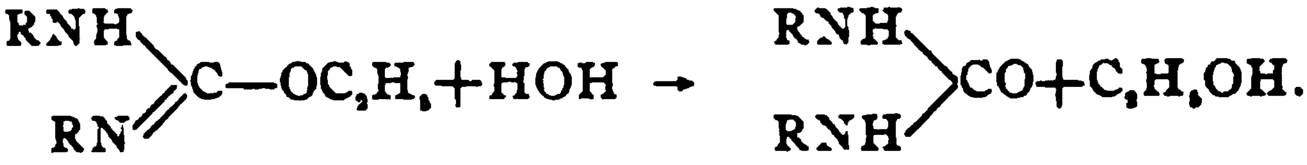
I.



$$\genfrac{}{}{0pt}{}{RN\diagdown}{RNH\diagup}C{-}OC_2H_5 + HCl \rightarrow \genfrac{}{}{0pt}{}{RNH\diagdown}{RNH\diagup}C{\genfrac{}{}{0pt}{}{\diagup Cl}{\diagdown OC_2H_5}} \rightarrow \genfrac{}{}{0pt}{}{RNH\diagdown}{RNH\diagup}CO + C_2H_5Cl.$$

This is the same reaction that occurs when the dry hydrochloride is heated, a quantitative splitting into dialphylurea and alkyl chloride.

II*a*.

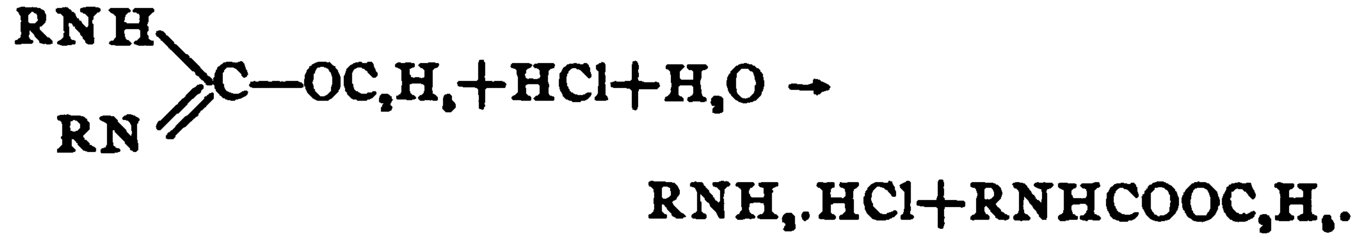


$$\genfrac{}{}{0pt}{}{RNH\diagdown}{RN\diagup}C{-}OC_2H_5 + HOH \rightarrow \genfrac{}{}{0pt}{}{RNH\diagdown}{RNH\diagup}CO + C_2H_5OH.$$

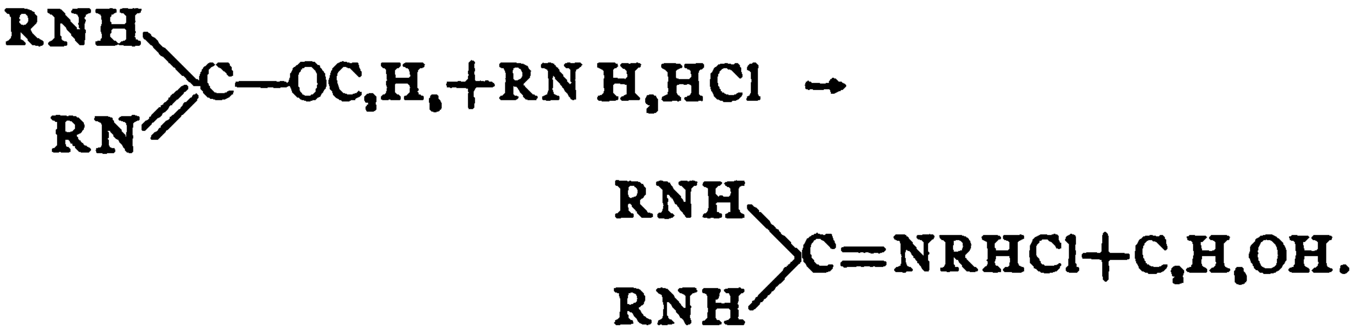
II*b*. $C_2H_5OH + HCl \rightarrow C_2H_5Cl + HOH.$

[1] *Am. Chem. J.*, 12, 493.

Carbanilide and alcohol are first formed by saponification, while the ethyl chloride is due to a reaction between the alcohol and hydrochloric acid.

IIIa.


$$\begin{matrix}RNH\\RN\end{matrix}\!\!>C-OC_2H_5+HCl+H_2O \rightarrow RNH_2.HCl+RNHCOOC_2H_5.$$

IIIb.


$$\begin{matrix}RNH\\RN\end{matrix}\!\!>C-OC_2H_5+RNH_2HCl \rightarrow \begin{matrix}RNH\\RNH\end{matrix}\!\!>C=NRHCl+C_2H_5OH.$$

IIIc. $RNHCOOC_2H_5+RNH_2HCl \rightarrow (RNH)_2CO+C_2H_5OH+HCl.$

$$C_2H_5OH+HCl \rightarrow C_2H_5Cl+H_2O.$$

This involves (*a*) the formation of aniline hydrochloride and phenyl urethane. These two compounds might, in turn, give carbanilide and alcohol as a primary reaction, while a small amount of the aniline hydrochloride reacts with unchanged isourea ether to form triphenylguanidine.

It will be noticed that III*a* and III*b* follow exactly the lines of decomposition of ordinary imido ethers.

When ethyl isodiphenylurea and one per cent. hydrochloric acid are heated at 100° for eight hours, the tubes open with slight pressure, due to ethyl chloride. The main product is carbanilide; traces of triphenylguanidine are also present.

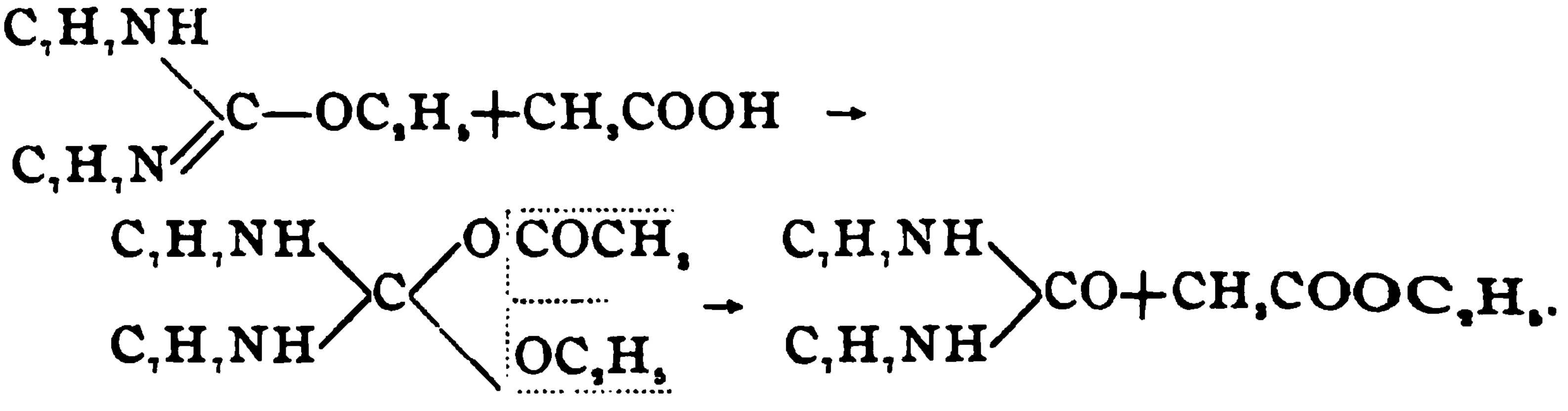
A test for alcohol with benzoyl chloride and caustic soda gave negative results. This shows that the reaction cannot proceed according to II. Since ethyl alcohol and aqueous hydrochloric acid do not give ethyl chloride, alcohol should be in the solution, but the above test proved its absence.

Bearing upon equation III are the following data: In one experiment the contents of the tube, after treatment with alkali, gave a few drops of oil which the bleaching-powder test showed to be aniline (III*a*). Between aniline and the urea ethers there is no reaction. (See below.)

When, however, ethyl isocarbanilide is heated with a dilute aqueous solution of aniline hydrochloride at 100°, traces of triphenylguanidine are obtained (III*b*). But when phenyl urethane and aniline hydrochloride were heated for eight hours in a sealed tube at 100°, the tube opened without pressure; no carbanilide and no ethyl chloride were obtained. The phenyl urethane was recovered unchanged; this disproves the possibility of III*c*. Hence the formation of carbanilide and ethyl chloride, the main products of the action of dilute aqueous hydrochloric acid on ethyl isocarbanilide, cannot proceed according to III. I alone accounts fully for the formation of these compounds. Equation I, therefore, positively represents the true action of aqueous hydrochloric acid on urea ethers in its principal phase. The formation of the by-product, triphenyl guanidine, takes place, as just shown, by the secondary reactions, III*a* and III*b*. These reactions bring out the radical point of difference between the imido ethers and the urea ethers. With the former, the reactions corresponding to III*a* and III*b* are the exclusive ones, or predominate.[1]

With the urea ethers, I has become the most prominent, while III*a* and III*b* are almost entirely absent.[2]

Action of Glacial Acetic Acid.—When a slight excess of glacial acetic acid was added to ethylisodi-*o*-tolylurea, the formation of a white solid and of ethyl acetate, recognized by its odor, was observed. The reaction was completed by heating in an oil-bath at 130° for a short time. When examined, the solid residue proved to be pure *o*-carbtoluide. The course of the reaction is as follows:



$$\begin{matrix}C_7H_7NH \\ C_7H_7N\end{matrix}\!\!>\!C{-}OC_2H_5 + CH_3COOH \rightarrow$$

$$\begin{matrix}C_7H_7NH \\ C_7H_7NH\end{matrix}\!\!>\!C\!<\!\begin{matrix}O\,COCH_3 \\ OC_2H_5\end{matrix} \rightarrow \begin{matrix}C_7H_7NH \\ C_7H_7NH\end{matrix}\!\!>\!CO + CH_3COOC_2H_5.$$

Addition of the acetic acid doubtless occurs, forming an inter-

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[1] A reaction according to I does not seem to be recorded in the literature of the ordinary imido ethers, but it is thought that a careful investigation will show that it takes place to a very small extent.

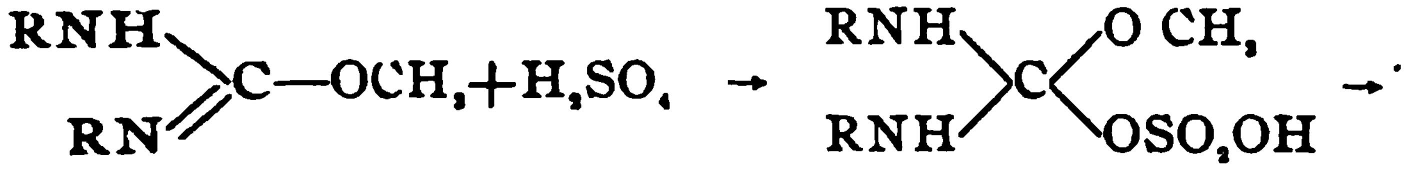
[2] These facts seem to shed valuable light on the constitution and behavior of the hydrochlorides of imido ethers and urea ethers. Their bearing on this subject will be discussed by Dr. Stieglitz in a paper on the subject in the *Am. Chem. J.*, 21, 101.

mediate acetate, which is too unstable to be isolated. This addition-product begins to decompose at ordinary temperatures, giving acetic ether and *o*-carbtoluide, a reaction analogous in every way to that with hydrochloric acid. Amylisodi-*o*-tolylurea and acetic acid slowly react at ordinary temperatures, and on warming to the boiling-point of the latter, decomposition is soon effected. Two products were obtained, *o*-ditolylurea, identified by its melting-point and properties, and amyl acetate, recognized by its odor.

Action of Dilute Sulphuric Acid.—Dilute sulphuric acid acts upon the isourea ethers less readily than hydrochloric acid. In the cold the complete decomposition is very slow. On heating methylisodi-*o*-tolylurea with five per cent. sulphuric acid in a sealed tube at 100°–110° for four hours, complete saponification followed. The tube opened without pressure. Much *o*-carbtoluide had crystallized out, and the clear solution gave no test for urea ether on heating with dilute hydrochloric acid.

Ammonium hydroxide gave a very slight precipitate—possibly of tritolylguanidine—but the amount was not sufficient for identification. The presence of methyl alcohol was shown by the benzoyl chloride test. The reaction evidently follows the same lines as that with dilute hydrochloric acid.

I*a*.



$$\begin{matrix} RNH \\ RN \end{matrix}\!\!>\!C{-}OCH_3 + H_2SO_4 \rightarrow \begin{matrix} RNH \\ RNH \end{matrix}\!\!>\!C\!<\!\begin{matrix} OCH_3 \\ OSO_2OH \end{matrix} \rightarrow$$

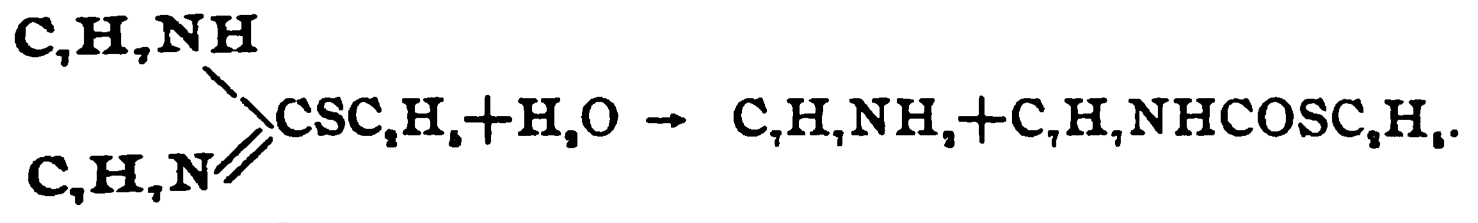
$$(RNH)_2CO + CH_3SO_4H.$$

I*b*. $CH_3SO_4H + H_2O \rightarrow CH_3OH + H_2SO_4.$

The relation of the decomposition here to that of the imido ethers is the same as in the preceding cases.

The action of strong sulphuric acid was tried in order to compare the relative behavior of oxygen and thiourea ethers. Will and Bielschauski[1] found that when ethylthiodi-*o*-tolyl urea was heated with twenty per cent. sulphuric acid at 160°–170° for three hours, incomplete saponification followed, with the formation of *o*-toluidine and monothio-*o*-tolyl urethane.

II.



$$\begin{matrix} C_7H_7NH \\ C_7H_7N \end{matrix}\!\!>\!CSC_2H_5 + H_2O \rightarrow C_7H_7NH_2 + C_7H_7NHCOSC_2H_5.$$

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[1] *Ber. d. chem. Ges.*, 13, 1317.

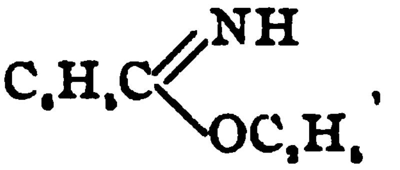
Ethyl isocarbanilide was heated under like conditions. The tube opened with pressure due to carbon dioxide. The contents of the tube, which formed a clear, dark-brown solution, were shaken out with ether. This yielded nothing, showing the absence of phenyl urethane. This acid solution, when neutralized, gave an oil which the bleaching-powder test proved to be aniline. Complete saponification according to

$$(C_6H_5N{:})C(NHC_6H_5)OC_2H_5+H_2SO_4+2H_2O \rightarrow (C_6H_5NH_3)_2SO_4+C_2H_5OH+CO_2$$

evidently takes place.

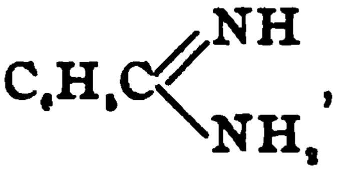
Carbanilide, the first saponification product according to p. 171, I, I found, is completely saponified by twenty per cent. sulphuric acid at 150°-160°, in the course of three hours. Phenyl urethane, the first saponification product to be expected according to the behavior of the thiourea ethers (p. 171, II) is, according to my observations, much more slowly decomposed under the same conditions, considerable urethane being recovered. There is no doubt, therefore, that even toward twenty per cent. sulphuric acid, at 160°, urea ethers first lose alcohol and not aniline, by saponification, in marked contrast to the thiourea ethers and ordinary imido ethers.

Action of Ammonia and Aniline.—Reference has been made[1] to what is doubtless one of the most characteristic reactions of the imido ethers; that is, the remarkable ease with which they react with ammonia or substituted amines in the cold or on warming slightly to form amidines. Thus, benzimido ether,



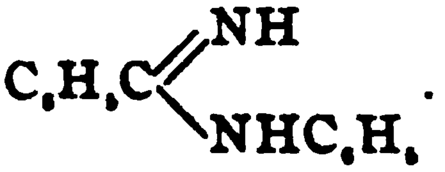
$$C_6H_5C{\begin{matrix}\diagup NH\\ \diagdown OC_2H_5\end{matrix}},$$

reacts readily and smoothly with ammonia to form benzamidine,



$$C_6H_5C{\begin{matrix}\diagup NH\\ \diagdown NH_2\end{matrix}},$$

and with aniline to form phenylbenzamidine,



$$C_6H_5C{\begin{matrix}\diagup NH\\ \diagdown NHC_6H_5\end{matrix}}.$$

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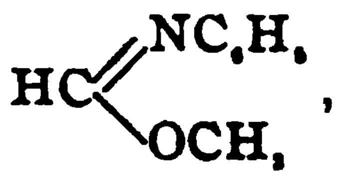
[1] Page 138.

Methyl isoformanilide,



$$HC\begin{matrix}\diagup NC_6H_5\\ \diagdown OCH_3\end{matrix},$$

with aniline or aniline hydrochloride gives a quantitative yield of diphenylformamidine,

$$HC\begin{matrix}\diagup NC_6H_5\\ \diagdown NHC_6H_5\end{matrix},$$

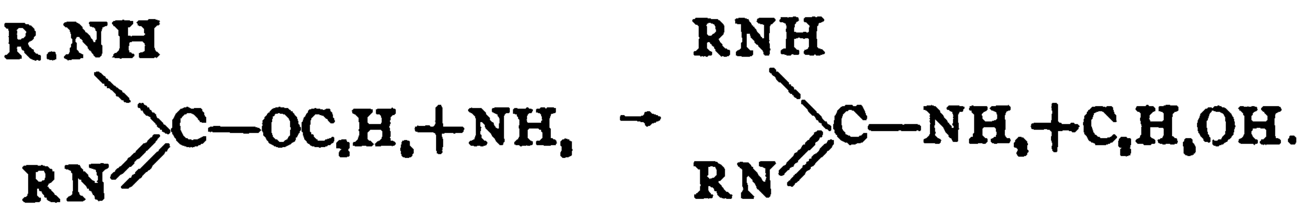
while the oxygen ethers of succinimide react with aniline with evolution of heat to form an amidine derivative.[1]

Judging then from analogy alone, the isourea ethers which contain this same grouping should react readily to form substituted guanidines. The results of the experiments directly contradicted this expectation, and showed the surprising stability of the isourea ethers toward basic reagents.

A solution of ethylisodiphenyl urea in alcoholic ammonia was heated at 130°–140° for several hours. The tube, which opened without pressure, contained an oil which was soluble in hydrochloric acid, and did not respond to any of the tests for aniline. On warming the acid solution, carbanilide and ethyl chloride were formed, showing that the oil consisted of unchanged urea ether. No trace of triphenylguanidine could be found in the acid filtrate.

When the ammoniacal solution was heated to 190°–200°, partial reaction occurred. Traces of diphenylguanidine were isolated, but most of the ether was unchanged.

On heating methylisodi-*o*-tolyl urea with alcoholic ammonia at 200° for three hours, a very incomplete conversion into di-*o*-tolylguanidine (m. p. 179°) took place.



$$\begin{matrix}R.NH\diagdown\\ RN\diagup\!\!\!\!\diagup\end{matrix}C—OC_2H_5+NH_3 \rightarrow \begin{matrix}RNH\diagdown\\ RN\diagup\!\!\!\!\diagup\end{matrix}C—NH_2+C_2H_5OH.$$

It has been previously shown[2] that ethylisodiphenyl urea and aqueous aniline hydrochloride at 100° give carbanilide and traces, but only *slight* traces, of triphenylguanidine. An effort

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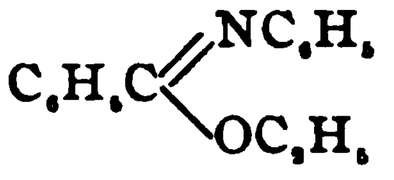
[1] Comstock and Wheeler: *Am. Chem. J.*, 13, 10.

[2] Page 169.

was made to prepare triphenylguanidine directly from the two substances. Molecular proportions of aniline and urea ether were heated in an oil-bath at 140°–150° for several hours. The oily product gave a test for aniline, and on warming with dilute hydrochloric acid, in which it dissolved, carbanilide was deposited, showing the presence of unchanged urea ether.

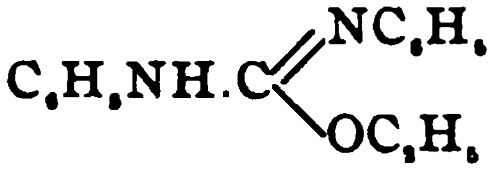
The acid filtrate contained no trace of triphenylguanidine. As there was no reaction at the temperature employed, the mixture was heated at 290°–300° for five hours. The tube which opened with pressure, was filled with combustible gases. It contained aniline, traces of urea ether, and a few crystals of carbanilide but no triphenylguanidine. The explanation of this will be seen in the action of heat upon the urea ether alone.

These experiments with ammonia and aniline show clearly the remarkable stability of the urea ethers, as compared with the imido ethers. The explanation for this must lie in the fact that the addition of an anilido group, C_6H_5NH, to the imido ether complex has made the molecule more positive. If more negative groups are introduced into a urea ether, as is the case with the ethoxy ether of dicarbethoxy urea, ammonia again reacts easily and smoothly with the formation of a guanidine.



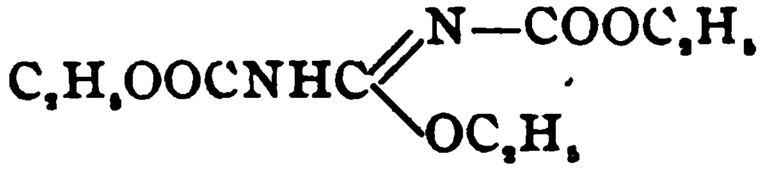
$$C_6H_5C\begin{cases}NC_6H_5\\OC_2H_5\end{cases}$$

reacts easily with ammonia and aniline.



$$C_6H_5NH.C\begin{cases}NC_6H_5\\OC_2H_5\end{cases}$$

reacts with ammonia with great difficulty, and not at all with aniline.



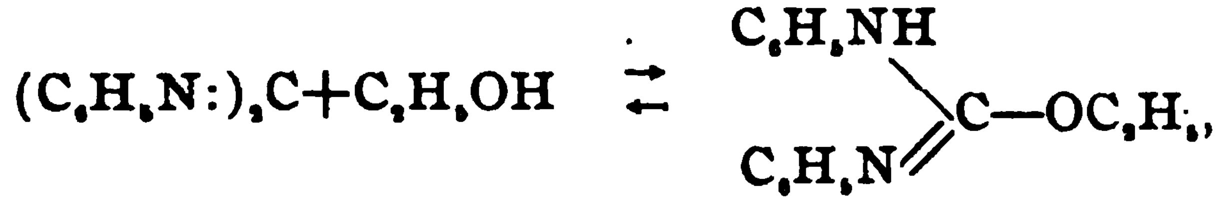
$$C_2H_5OOCNHC\begin{cases}N{-}COOC_2H_5\\OC_2H_5\end{cases}$$

reacts easily with ammonia.

This same effect of increasing the negative nature of the molecule is seen in the behavior of the thiourea ethers. Here a much greater activity is noticed. Thus ethylthiodiphenyl urea reacts at 120° with alcoholic ammonia to form mercaptan and diphenylguanidine[1] while boiling with aniline is sufficient to convert methylthioditolyl urea into phenylditolylguanidine and methylsulphhydrate.[2]

Action of Heat upon the Urea Ethers.—The results of the last experiment with aniline and urea ether led to trying the effect of heat alone.

Ethylisodiphenyl urea was heated for five hours at 295°–300°, and a gas, ethylene, escaped, which burned with a luminous flame. The residue, which was a semisolid mass mixed with crystals, consisted of carbanilide and polymerized carbodiphenylimide. The formation of polymerized carbodiphenylimide in this reaction would indicate that the decomposition of ethyl isocarbanilide is not directly into ethylene and carbanilide, which gives phenyl isocyanate, but no carbodiphenylimide. It is, then, far more likely that at this high temperature the isocarbanilides are decomposed back into carbodiphenylimide and alcohol, the reaction by which they are formed being reversed;[3]



$$(C_6H_5N:)_2C+C_2H_5OH \rightleftarrows \begin{matrix} C_6H_5NH \\ C_6H_5N \end{matrix}\!\!>C—OC_2H_5,$$

and the alcohol breaking down partly into ethylene and water, the latter combines with the carbodiimide to form carbanilide.[4]

Action of Potassium Hydroxide.—A solution of methyliso-*o*-carbtoluide in strong alcoholic potash is not decomposed by long standing or even by boiling.[5] The recovered oil responded to the tests for the urea ethers. Some of the urea ether, dissolved in alcoholic potash, was heated in a sealed tube at 160° for three hours. The tube opened without pressure. When the alcoholic solution was acidified with hydrochloric acid there was an evolution of carbon dioxide; no unchanged urea ether was found. The solution contained, however, an oil soluble in the acid.

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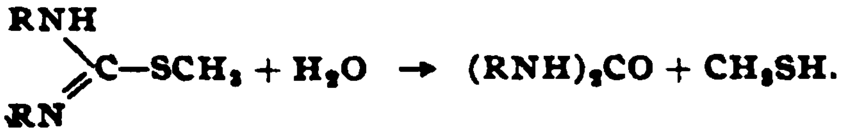
[1] Rathke: *Ber. d. chem. Ges.*, 14, 1776.

[2] *Ibid.*, 15, 1309.

[3] Page 140.

[4] Ethyl thiocarbanilide (or toluide) breaks down in like manner on heating into ethylmercaptan and carbodiphenylimide.

[5] Methyl thiocarbanilide breaks down into carbanilide and mercaptan when boiled with alcoholic potash.

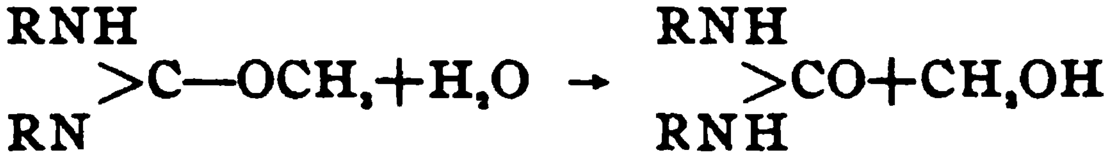


$$\begin{matrix} RNH \\ RN \end{matrix}\!\!>C—SCH_3 + H_2O \rightarrow (RNH)_2CO + CH_3SH.$$

Will: *Ber. d. chem. Ges.*, 14, 1489.

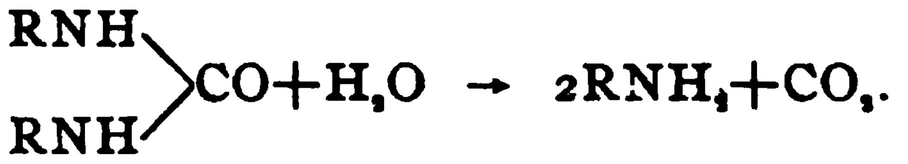
This, with benzoyl chloride, gave *o*-benztoluide (m. p. 143°) and was, therefore, *o*-toluidine. Methylisodi-*o*-tolyl urea shows the same stability toward boiling ten per cent. caustic soda. No saponification follows.[1] When heated with the aqueous alkali for three hours at 160° the decomposition was complete. The carbon dioxide was absorbed by caustic soda and the *o*-toluidine identified by changing into *o*-benztoluide. The clear solution contained methyl alcohol. This was shown by the benzoyl chloride test. The reaction can doubtless be represented as follows :

a.



$$\begin{matrix}RNH\\ RN\end{matrix}>C{-}OCH_3+H_2O \rightarrow \begin{matrix}RNH\\ RNH\end{matrix}>CO+CH_3OH$$

b.



$$\begin{matrix}RNH\\ RNH\end{matrix}>CO+H_2O \rightarrow 2RNH_2+CO_2.$$

Experiment showed that a dialphyl urea, such as carbanilide, was readily and completely saponified at 160° by ten per cent. aqueous or alcoholic potash.

These experiments have brought out incidentally the relative stability toward acids and alkalies of the oxygen and thiourea ethers. By hydrochloric, sulphuric, and acetic acids,[2] the oxygen ethers are gradually decomposed in the cold, but readily when heated, while the opposite is true of the thiourea ethers. Thus, methyl thiocarbanilide can be boiled with strong hydrochloric acid without change; decomposition[3] into aniline and mercaptan is only effected by heating with concentrated acid at 150°. With basic reagents the oxygen ethers show a much greater stability.

Previous experiments have shown their inertness[4] toward ammonia, aniline, and caustic alkalies. On the other hand, the same reagents react with relative ease with the thiourea ethers.[5]

Action of Hydrogen Sulphide.—Many of the experiments thus far described have borne directly upon the relation between the urea ethers, the imido ethers, and the thiourea ethers. It must

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[1] Ethyl isocarbanilide heated at 120°-130° for six hours, under like conditions, gave mainly unchanged urea ether, only traces of aniline, and no carbanilide.

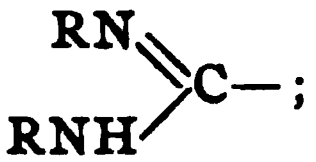
[2] Pages 166, 171, 170.

[3] Weith : *Ber. d. chem. Ges.*, 14, 1490.

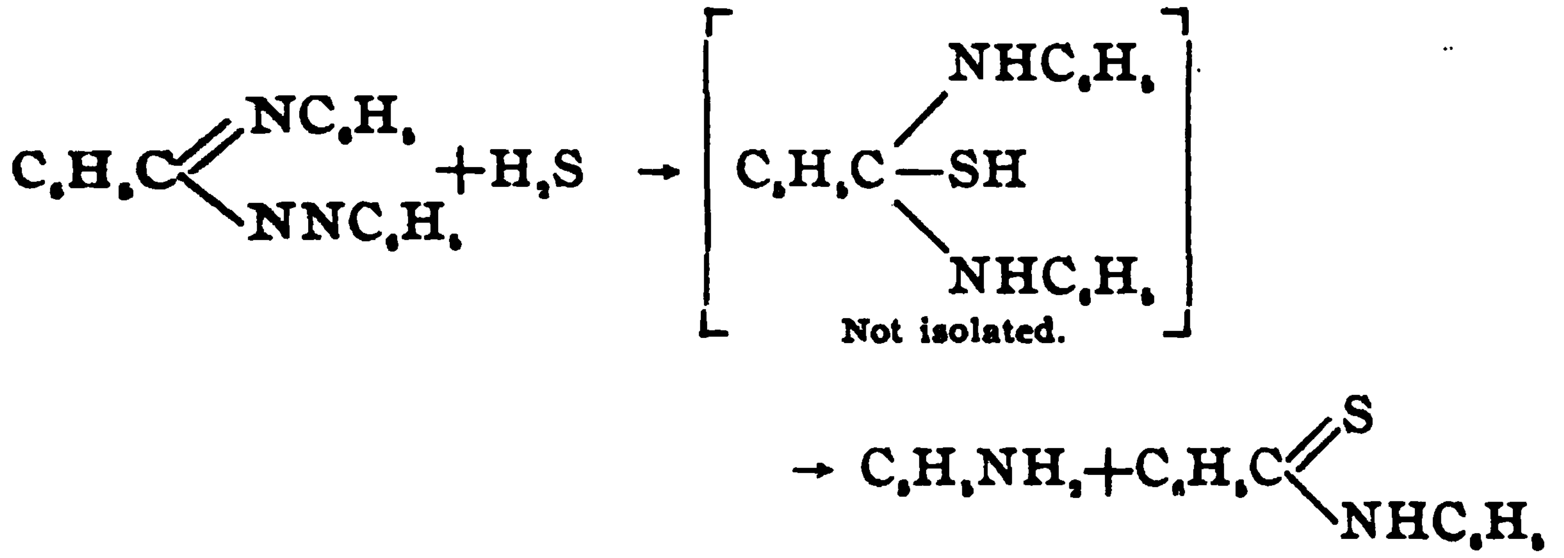
[4] Pages 172 and 175.

[5] *Ber. d. chem. Ges.*, 14, 1489 and 1490.

not be forgotten that the urea ethers contain also the amidine grouping



and hence could show some of the typical reactions of the amidines. Bernthsen[1] has found that there are two reagents, hydrogen sulphide and carbon disulphide, that react in an especially characteristic manner with this class of compounds. Thus, if α-benzenyldiphenylamidine is heated at 160°–165° in a stream of dry hydrogen sulphide, there is a quantitative splitting into aniline and thiobenzanilide.



The carbon disulphide reaction, which is somewhat similar, will be discussed later.

Dry hydrogen sulphide was passed over ethylisodiphenyl urea in a distilling bulb immersed in an oil-bath. This was connected with another distilling bulb, which served as a receiver, while the gaseous products of the reaction were led over alcoholic ammonia for the purpose of absorbing any carbon disulphide that might be formed. At 130°–140° there was no reaction, the urea ether remaining unchanged. When the temperature was raised to 180°–190° slow decomposition began. A few drops of oil distilled over in the receiver. This was soluble in hydrochloric acid, and responded to the bleaching-powder test for aniline, and with benzoyl chloride gave benzanilide. A slight residue of carbanilide was left in the distilling bulb. When the solution of alcoholic ammonia was evaporated to dryness and the residue taken up with water, it gave, with ferric chloride, a test for ammonium thiocyanate, showing that car-

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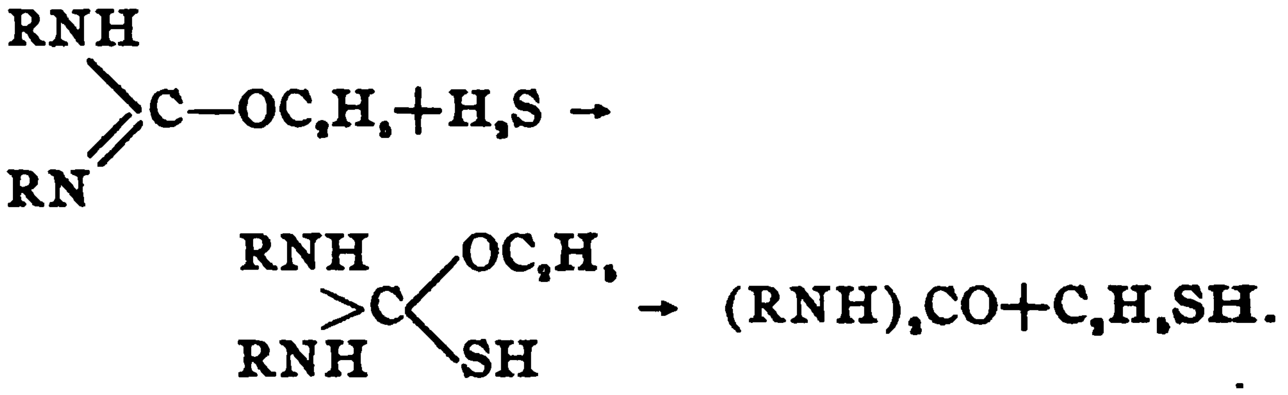
[1] *Ann. Chem.* (Liebig), 192, 32.

bon disulphide had been absorbed. Mercaptan, C_2H_5SH, was recognized among the gaseous products by its odor. Any reaction, then, must take into account the formation of these compounds: carbanilide, aniline, carbon disulphide, and mercaptan.

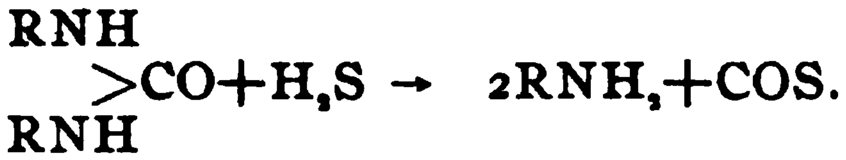
Three possibilities are open to consideration :

I*a*.



$$\begin{matrix}RNH\\ RN\end{matrix}\!\!>\!C-OC_2H_5+H_2S \rightarrow \begin{matrix}RNH\\ RNH\end{matrix}\!\!>\!C\!<\!\begin{matrix}OC_2H_5\\ SH\end{matrix} \rightarrow (RNH)_2CO+C_2H_5SH.$$

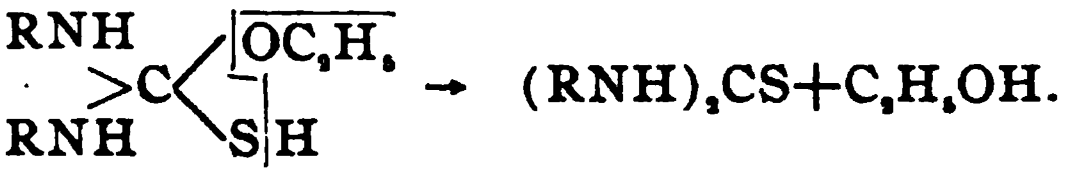
I*b*.



$$\begin{matrix}RNH\\ RNH\end{matrix}\!\!>\!CO+H_2S \rightarrow 2RNH_2+COS.$$

The hydrogen sulphide, which is a weak acid, acts in this case like hydrogen chloride, the unstable addition-product breaking down.

II*a*.

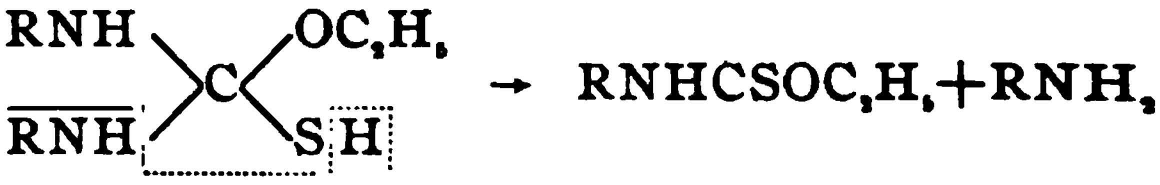


$$\begin{matrix}RNH\\ RNH\end{matrix}\!\!>\!C\!<\!\begin{matrix}OC_2H_5\\ SH\end{matrix} \rightarrow (RNH)_2CS+C_2H_5OH.$$

II*b*. $(RNH)_2CS+H_2S \rightarrow 2RNH_2+CS_2$.

Here ethyl alcohol is lost, instead of mercaptan, from the addition-product, giving thiocarbanilide.

III*a*.



$$\begin{matrix}RNH\\ RNH\end{matrix}\!\!>\!C\!<\!\begin{matrix}OC_2H_5\\ SH\end{matrix} \rightarrow RNHCSOC_2H_5+RNH_2$$

III*c*. $RNHCSOC_2H_5+H_2S \rightarrow RNH_2+CS_2+C_2H_5OH$.

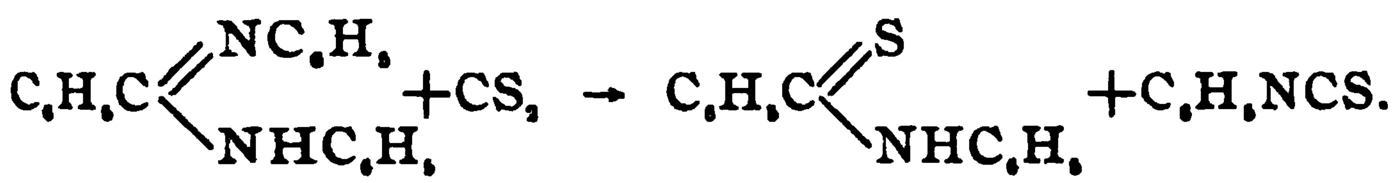
The intermediate phenylthiourethane is saponified in much the same way as with dilute acids. It will be noticed that III is the only one in which the normal decomposition of amidines is followed out.

The formation of mercaptan and carbanilide proves that the reaction certainly proceeds, to some extent, according to I*a*. That this could also account for some of the aniline was shown by a special experiment.

Carbanilide at 190° was found to be *very slowly* attacked by hydrogen sulphide with the formation of aniline (I*b*). The exceeding slowness of this reaction, however, as compared with the action of hydrogen sulphide upon the urea ethers, makes it certain that reaction II or III, or both, must occur.

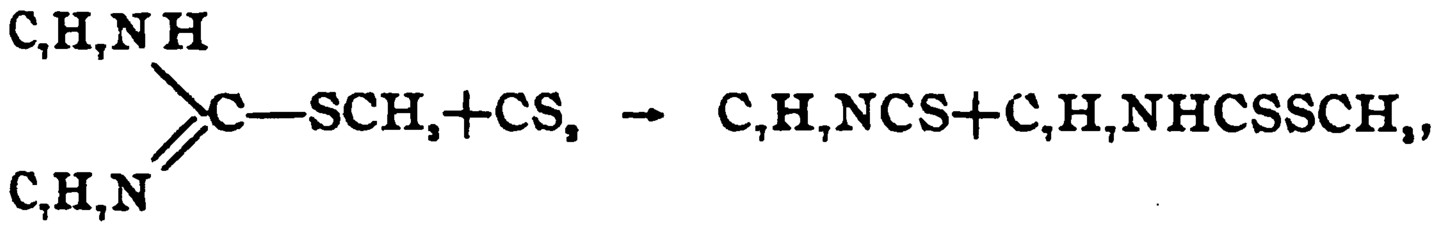
No further experimental evidence was obtained on this point; but the general fact that the urea ethers lose much more readily the alkyl group giving carbanilides[1] than an aniline group giving urea ethers, would be in favor of II.

Action of Carbon Disulphide.—When benzenyldiphenylamidine is heated with carbon disulphide at 130°–140°, there is formed thiobenzanilide and phenyl mustard oil.



$$C_6H_5C\begin{matrix}\nearrow NC_6H_5\\ \searrow NHC_6H_5\end{matrix} + CS_2 \rightarrow C_6H_5C\begin{matrix}\nearrow S\\ \searrow NHC_6H_5\end{matrix} + C_6H_5NCS.$$

The double bond is the point of attack with consequent loss of the imido group. Will and Beilschauski[2] have investigated the action of carbon disulphide upon the thiourea ethers.[3] They have shown, for instance, that methylthio-*p*-tolyl urea, heated with carbon disulphide at 180°, yields *p*-tolyl mustard oil and *p*-tolyldithiourethane,



$$\begin{matrix}C_7H_7NH\\ C_7H_7N\end{matrix}\!\!>\!C—SCH_3 + CS_2 \rightarrow C_7H_7NCS + C_7H_7NHCSSCH_3,$$

a result analogous, in all respects, to that with a true amidine. Other thio-ethers behave in a similar manner.

Ethylisodiphenyl urea was heated with carbon disulphide at 170° for six hours. The tube opened with pressure due to combustible gases. These slowly precipitated silver sulphide from a silver nitrate solution due to the presence of carbonyl sulphide (COS). The contents of the tube, which consisted of a solid mixed with an oil, were washed out with ligroin. The solid, after crystallization from alcohol, proved to be thiocarbanilide. The ligroin, after evaporation, left an oil with the odor of phenyl mustard oil. That it was the mustard oil was proved by the fact that it reacted directly with alcoholic ammonia, giving

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[1] Weith has shown that thiocarbanilide and hydrogen sulphide at 170° give a quantitative yield of aniline and carbon disulphide. *Ber. d. chem. Ges.*, 7, 1304.

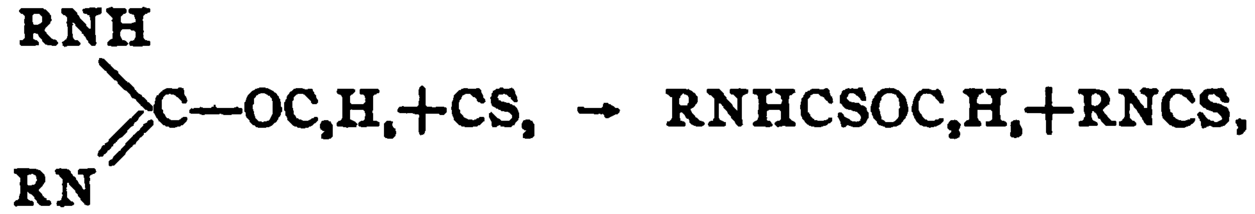
[2] Bernthsen: *Ann. Chem.* (Liebig), 192, 32.

[3] *Ber. d. chem. Ges.*, 15, 1317.

monophenylthiourea, and with aniline to form thiocarbanilide.

Methyliso-*o*-tolyl urea was heated under like conditions with carbon disulphide. The tube opened with pressure due to inflammable gases that slowly precipitated silver sulphide. The contents of the tube consisted of *o*-tolyl mustard oil and *o*-thiocarbtoluide, which were separated and identified as in the previous experiment. If the reaction proceeded as with other amidines, it would be formulated as follows :

I.



$$\begin{matrix}\text{RNH} \\ \text{RN}\end{matrix}\!\!>\!C{-}OC_2H_5 + CS_2 \rightarrow RNHCSOC_2H_5 + RNCS,$$

giving phenyl mustard oil ; and the β-thiourethane which was not isolated would have to break down according to

$$\text{II.}\quad 2.RNHCSOC_2H_5 \rightarrow (RNH)_2CS + COS + (C_2H_5)_2O$$

into thiocarbanilide, carbon oxysulphide, and ether.[1]

The action on silver nitrate indicated carbon oxysulphide, and the correctness of this equation, and thereby of the whole interpretation, was proved as follows :

Pure β-thiophenylurethane[2] was heated in a sealed tube at 170°–180° for six hours. The tube opened with pressure due to inflammable gases that slowly precipitated silver sulphide from a silver nitrate solution. The contents consisted of a little phenyl mustard oil formed by simple dissociation of the urethane,

$$C_6H_5NHCSOC_2H_5 \rightarrow C_6H_5NCS + C_2H_5OH,$$

and of thiocarbanilide. The decomposition occurs as already pointed out in equation II.

The same products were obtained when β-thiophenylurethane was heated in carbon disulphide solution. The experiments indicate that with a neutral reagent like carbon disulphide, the oxygen-urea ethers lose an imide group behaving, in all respects, like a true amidine.

The thiourea ethers react in this same way, the only difference being in the stability of the dithiourethane formed.

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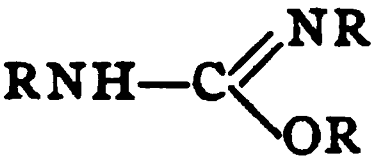
[1] Dithiophenylurethane, $C_6H_5NHCSSC_2H_5$, formed by the action of carbon disulphide on the thio-ethers, is stable at this temperature.—*Ber. d. chem. Ges.*, 15, 1317.

[2] The decomposition of the thiourethane will be further investigated and the results published in a later paper.

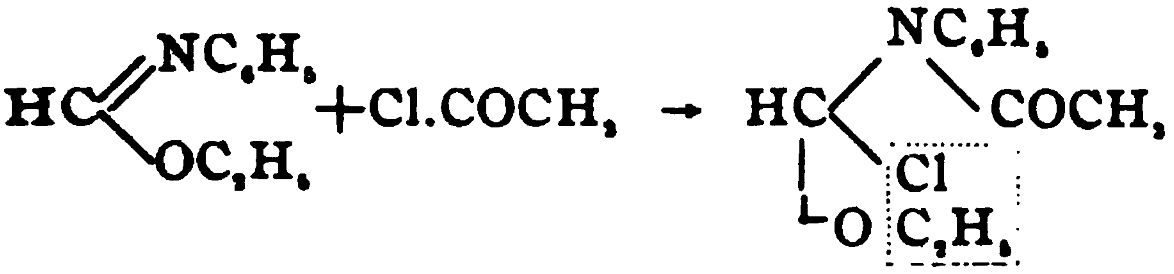
The Action of Acyl Chlorides upon the Urea Ethers.—Bodies of the type



$$RNH—C\begin{matrix}\nearrow NR \\ \searrow OR\end{matrix}$$

present toward acyl chlorides, two points of attack, the double bond and the hydrogen attached to the anilido group, which ought to be easily replaced by an acyl group, since the body is a strong base; *i. e.*, anilidophenylimidoformic ether.

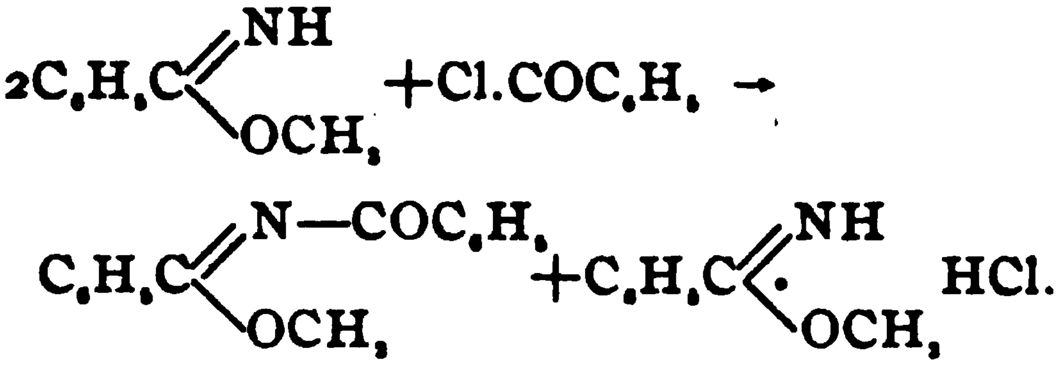
Wheeler and Walden[1] have made a most interesting discovery that the acyl chlorides act on phenylimido esters easily and smoothly, acetyl chloride giving with phenylimidoformic ester, acetylformanilide and ethyl chloride. They have formulated the reaction as follows:



$$HC\begin{matrix}\nearrow NC_6H_5 \\ \searrow OC_2H_5\end{matrix}+Cl.COCH_3 \rightarrow HC\begin{matrix}\nearrow NC_6H_5\searrow COCH_3 \\ \searrow Cl \\ \llcorner O\ C_2H_5\end{matrix}$$

$$\rightarrow (HCO)N(C_6H_5)(COCH_3)+ClC_2H_5.$$

On the other hand, they found that benzimidomethyl ester containing an imide group, NH, with a replaceable hydrogen atom reacts according to



$$2C_6H_5C\begin{matrix}\nearrow NH \\ \searrow OCH_3\end{matrix}+Cl.COC_6H_5 \rightarrow$$

$$C_6H_5C\begin{matrix}\nearrow N—COC_6H_5 \\ \searrow OCH_3\end{matrix}+C_6H_5C\begin{matrix}\nearrow NH \\ \searrow OCH_3\end{matrix}HCl.$$

The intermediate addition-product loses hydrogen chloride, which immediately unites with a second molecule of the more basic free imido ether to form a salt. The product then contains equal molecules of benzimidomethyl ester hydrochloride and benzoylbenzimidomethyl ester.[2]

If freshly distilled acetyl chloride (a slight excess over one molecule) is added to a benzene solution of ethyl isocarbanilide (one molecule), reaction soon begins. The use of a neutral sol-

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[1] *Am. Chem. J.*, 19, 130.

[2] Wheeler and Walden: *Ibid.*, 19, 136.

vent is necessary in order to control the action. After standing for thirty-six hours, the benzene was filtered from a white solid that had crystallized out. This, on examination, proved to be pure carbanilide; there was no trace of any hydrochloride or salt of any base. The solution when evaporated directly yielded acetyldiphenylurea, a body previously described by McCreath.[1]

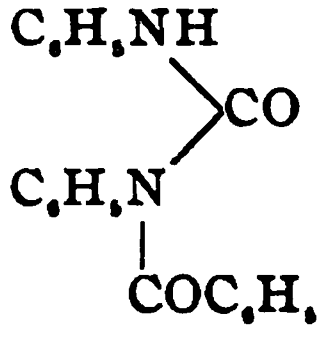
When ethylisodiphenylurea and benzoyl chloride are mixed, there is no reaction at first, but on standing for a short time, the mixture warms up and becomes semisolid. It is better, however, to dissolve the urea ether in benzene, add the benzoyl chloride, and allow the solution to stand two or three days. A white solid is slowly deposited; this, as in the previous case, was found to be pure carbanilide, with no admixture of any other body. The solution, on evaporation, gave a new compound, benzoyldiphenylurea, which was purified by recrystallization from ligroin (40°–60°) and alcohol.

Analysis:[2]

0.1027 gram substance gave 8.4 cc. moist nitrogen at 21.5° and 748.3 mm.

	Calculated for $C_{20}H_{16}N_2O_2$.	Found.
Nitrogen	8.86	9.18

Benzoyldiphenylurea,



is insoluble in water, and easily soluble in ordinary organic solvents. It crystallizes in fine white needles, which melt at 131°. When heated a little above its melting-point, it dissociates, giving benzanilide and phenyl isocyanate, a reaction which also characterizes monacetylcarbanilide. These bodies, which can be prepared by the action of phenyl isocyanate upon the anilides,[3] are relatively unstable, and dissociate easily into their components.

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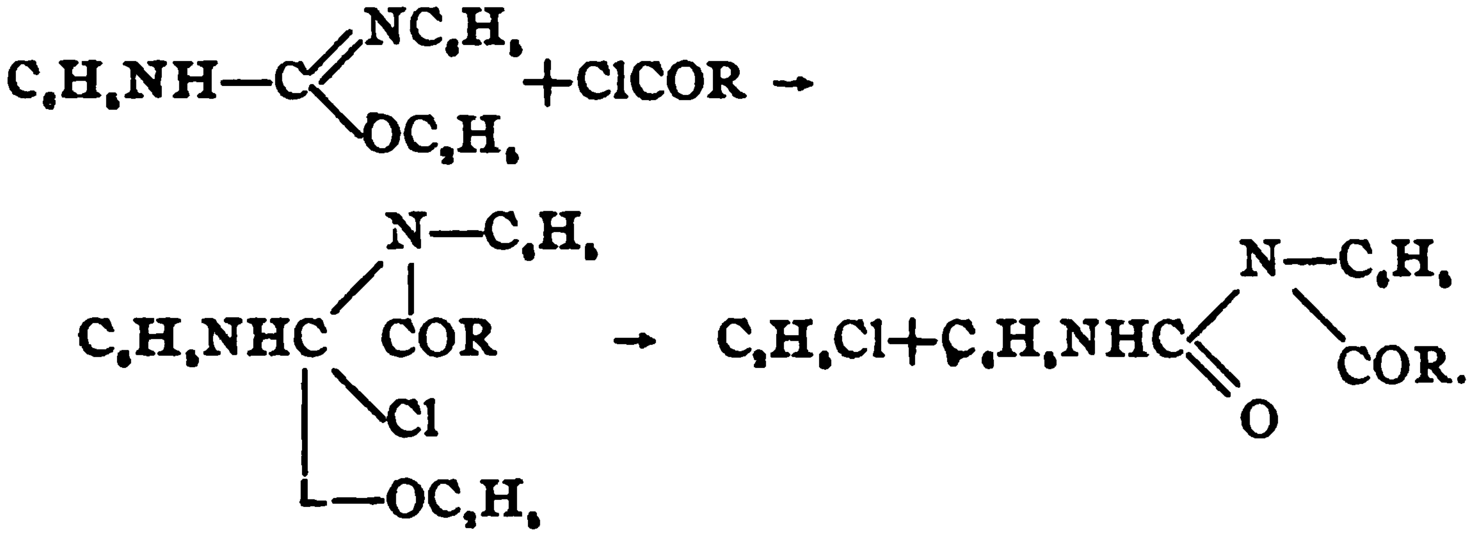
[1] *Ber. d. chem. Ges.*, 8, 1181; Kuhn: *Ibid.*, 17, 2282.

[2] This analysis was kindly made for me by Mr. M. D. Slimmer, of this laboratory.

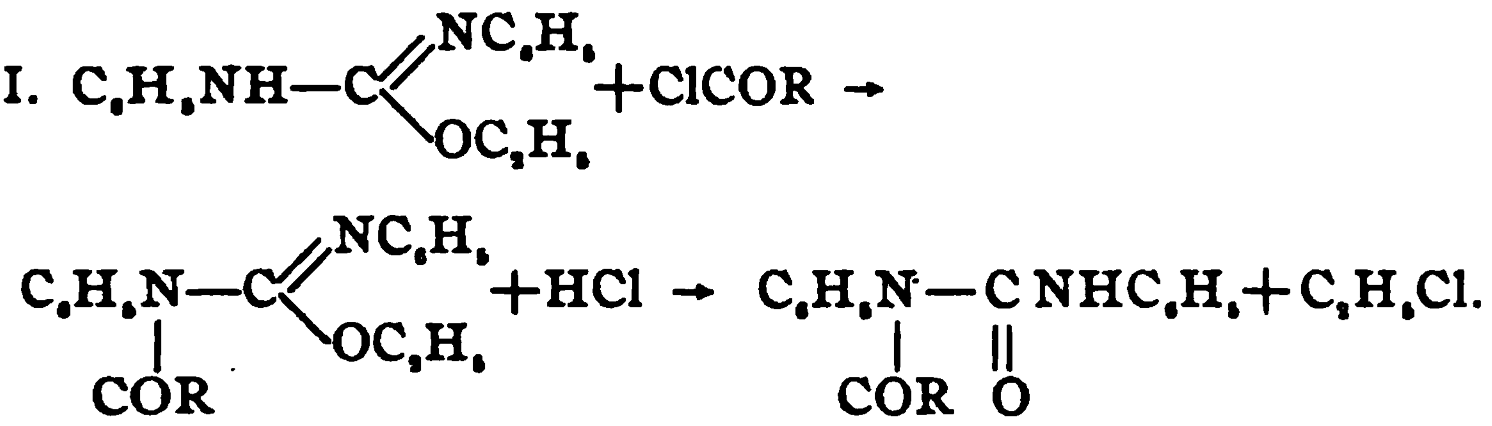
[3] McCreath: *Ber. d. chem. Ges.*, 8, 1181.

Since the isourea ethers possess two points of attack, the formation of these acyldiphenylureas can be explained in two ways:

I.



II.



In one the acyl chloride adds to the double bond, the usual point of attack in imido ethers, but the very unstable addition-product loses ethyl chloride, giving the monacyldiphenylurea. The formation of carbanilide is doubtless due to traces of free acid in the acyl chloride.[1] These results correspond in every way to the action of acid chlorides on the phenylimido ethers.[2]

While the reaction most probably proceeded according to I, the second possibility had to be considered. Here the anilido hydrogen is replaced by the acyl group, while the free hydrochloric acid reacts with an acylurea ether, splitting off ethyl chloride and so giving the same end-products. The ease with which the urea ethers unite with dry hydrogen chloride has been set forth before. These hydochlorides are stable at ordinary temperatures in the absence of moisture.[3] For this reason, if any hydrochloric acid was set free, it would immediately unite with another molecule of urea ether to form the urea ether hydrochloride insoluble in the solvent used. This is shown also

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[1] Page 182.

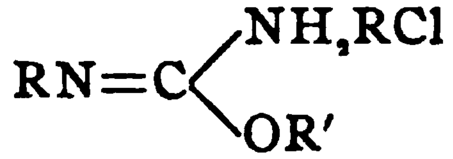
[2] *Am. Chem. J.*, 29, 130.

[3] Page 141.

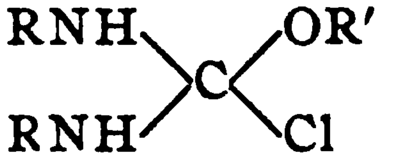
by the behavior already referred to, of benzimidomethyl ester and benzoyl chloride.[1]

The absence of any hydrochloride of the urea ether or of any acyl urea ether leaves the second (II) interpretation of the action of acyl chlorides without a single experimental piece of evidence in its favor, and makes the first (I) the more probably correct one. The reaction is of some importance, since it must be considered as throwing some light on the constitution of the salts—such as the hydrochlorides— of the urea ethers.[2]

For these compounds two constitutions are possible:

A.


$$RN{=}C\left\langle\begin{matrix}NH_2RCl\\OR'\end{matrix}\right.$$

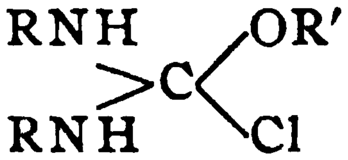
B.


$$\left.\begin{matrix}RNH\\RNH\end{matrix}\right\rangle C\left\langle\begin{matrix}OR'\\Cl\end{matrix}\right.$$

One would certainly think that if the basicity of the urea ethers was due to the aniline groups forming ammonium salts (A), that the basic anilido group, C_6H_5NH, would also show the other characteristic reaction of such a group in a basic molecule; *viz.*, the ready formation of an acyl derivative,

$$C_6H_5N(COC_6H_5)C(:NC_6H_5)OC_2H_5,$$

but no such compound could be obtained, although it was with the intention of preparing it, that this reaction was first undertaken and then studied. On the other hand, the formation of the compounds actually obtained,—acyl carbanilide and ethyl chloride—is according to I clearly in close agreement with the conception of the urea ether salts as having the constitution

B.


$$\left.\begin{matrix}RNH\\RNH\end{matrix}\right\rangle C\left\langle\begin{matrix}OR'\\Cl\end{matrix}\right.$$

Indeed where the imido ether grouping, —C(:NR)OR, is missing, acyl chlorides have hardly any effect. Thus, when carbanilide and benzoyl chloride are heated to 130°–140° in an oil-bath,

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[1] Page 181.

[2] See also Stieglitz : *Am. Chem. J.*, 21, 101.

the diphenyl urea goes into solution, but on cooling it crystallizes out unchanged.[1]

V. CARBONYLDIURETHANE.

The urea ethers thus far investigated have a phenyl or tolyl group and are basic enough to form definite salts with, and neutralize, acids. It seemed now of interest to ascertain in what way the ethers of ureas would behave were the phenyl group replaced by one still more strongly negative, such as carbethoxy or acyl. Such a urea would possess the grouping,

$$RCONHCONHCOR,$$

analogous to that in the uric acids, and, in consequence, its reactions should throw some light upon those of the latter series.

A starting-point for the preparation of ethers of such a urea presents itself in carbonyldiurethane,

$$CO(NHCOOC_2H_5)_2$$

(dicarbethoxyurea), a compound whose constitution has been definitely determined, so that no question need arise on that score. This body, together with its silver salt, was prepared in this laboratory,[2] by Folin, who worked under the direction of Dr. Stieglitz. He found that carbonyldiurethane gave a monosilver salt, probably

$$(AgO)C(:NCOOR)(NHCOOR).$$

Such a body would present an excellent opportunity for preparing such isourea ethers by means of alkyl iodide, and on the other hand, the formation of such ethers with the constitution

$$(RO)C(:NCOOR)(NHCOOR),$$

would be a complete confirmation of the constitution of the silver salt. With this twofold object, the action of alkyl iodide was investigated by me.

An isourea ether with the above composition was obtained without difficulty, its constitution determined beyond a doubt, and important changes in the chemical behavior of isourea

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[1] At higher temperatures (160°-170°) there is a reaction, the results of which will be described in a later paper. The study of the action of acyl chlorides and anhydrides on the dialphylureas and thioureas, is being continued by me (Dains).

[2] *Am. Chem. J.*, 19, 348.

ethers, with the more negative carbethoxy groups, COOR, attached to the nitrogen observed.

Preparation of Carbonyldiurethane.—Folin ascertained that carbonyldiurethane was the main product when a mixture of one molecule of phosgene, two molecules of urethane, and two molecules of pyridine were heated in a sealed tube at 85° for thirty minutes. A more simple method of preparation, and one that does not involve the use of a sealed tube, is as follows: A mixture is made of two molecules each of urethane and pyridine; a little benzene is used, if necessary, to complete the solution. A flask containing a ten per cent. solution of phosgene (one molecule), in benzene and connected with an ice-cooled condenser, is surrounded with a freezing-mixture. On adding the urethane solution slowly to the phosgene, immediate reaction occurs, and a reddish solid separates out on the sides of the flask. After standing an hour the freezing-mixture is replaced by water, which is slowly warmed to the boiling-point of benzene. This latter temperature is maintained for an hour. When cold, the liquid in the flask separates into two layers, the upper of benzene, the lower a dark red oil which slowly becomes semisolid, owing to the crystallization of the carbonyldiurethane. On examination, the upper layer was found to contain very little carbonyldiurethane, the most of it being in the red oil at the bottom. This latter, after treatment with water, was warmed to drive off traces of benzene, and cooled in a freezing-mixture, the carbonyldiurethane readily crystallizing out. On concentrating the filtrate and again cooling, a second crop of crystals can be obtained while extraction with ether removes the remainder. The product is best purified by crystallization from water. The yield is about seventy per cent. of the theory. With a sealed tube Folin had obtained a forty per cent. yield. The presence of the pyridine, which absorbs the hydrochloric acid set free, greatly facilitates the reaction. A benzene solution of phosgene and urethane alone does not react at the boiling-point of the benzene.

Carbonyldiurethane is very stable toward acids.[1] Fixed caustic alkalies dissolve it with the formation of soluble salts. For synthetic use the silver and sodium salts of carbonyldiureth-

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[1] Folin: *Am. Chem. J.*, 19, 348.

ane were prepared, the first by Folin's method,[1] the latter as follows:

A concentrated solution of sodium ethylate—one molecule—was added to a solution of carbonyldiurethane, dissolved in as little absolute alcohol as possible. A gelatinous precipitate formed, which soon changed to a fine white crystalline powder. From more dilute solutions ether throws down the sodium salt. This was washed with absolute alcohol and ether, dried in a vacuum, and analyzed.

0.5800 gram substance gave 0.1790 gram sodium sulphate.

	Calculated for $C_7H_{11}N_2O_6Na$.	Found.
Sodium	10.18	10.00

No Disodium Salt Could be Obtained.—The monosodium salt, is formed only with a considerable excess of sodium ethylate. It is readily soluble in water and dilute alcohol. From a concentrated water solution of the sodium salt, lead nitrate precipitated the lead salt, but as this was found to be very unreactive with alkyl iodide, it was not further investigated.

With copper sulphate it gave not copper carbonyldiurethane, but a hydrated copper hydroxide, showing that the sodium salt is hydrolyzed in solution. The constitution of these salts will be discussed later.

The Action of Alkyl Iodide upon the Silver Salt.—The silver salt was suspended in dry ether and a slight excess over one molecule of ethyl iodide added. After standing for several days the ether was filtered from the silver iodide. On evaporation there is obtained an oil mixed with a little carbonyldiurethane. The oil was purified by washing with dilute alkali, and by solution in ligroin (b. p. 40°–60°), which dissolves only the oil. The excess of solvent was allowed to evaporate in a vacuum desiccator over vaseline and sulphuric acid. The resulting product is the ethoxy ether of carbonyldiurethane,

$$(C_2H_5O)C(:NCOOC_2H_5)NHCOOC_2H$$

(ethylisodicarbethoxyurea). It is a colorless mobile oil with a pleasant odor, easily soluble in ordinary neutral organic solvents, insoluble in water and insoluble in dilute alkalies. At ordinary

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[1] Folin: *Am. chem. J.*, 19, 350.

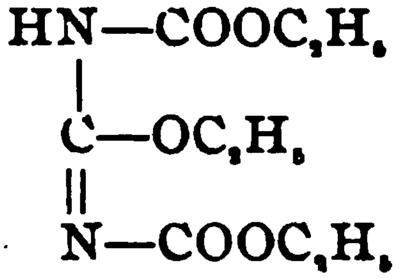
pressures it cannot be distilled without complete decomposition.

Analysis :

0.2444 gram substance gave 26.8 cc. moist nitrogen at 24° and 755 mm.

	Calculated for $C_9O_5H_{16}N_2$.	Found.
Nitrogen	12.07	12.30

Traces of the isomeric nitrogen ether are often found, showing that the reaction is not wholly one of direct replacement of the silver atom. If any nitrogen ether is present a carbylamine odor is obtained when the ether is decomposed with strong sulphuric acid and then warmed with alcoholic potash and chloroform. That the composition of the oil is



$$\begin{array}{l} HN{-}COOC_2H_5 \\ | \\ C{-}OC_2H_5 \\ \| \\ N{-}COOC_2H_5 \end{array}$$

(ethylisodicarbethoxyurea) is shown by its reactions with hydrochloric acid and alcoholic ammonia.

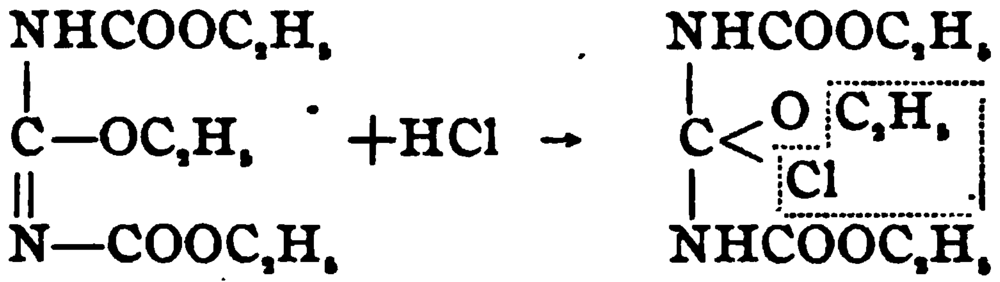
Action of Hydrochloric Acid on Ethylisodicarbethoxyurea.— When dry hydrogen chloride is passed over the ethoxy ether in a test-tube connected with an azotometer, ethyl chloride is split off quantitatively and is collected in the azotometer over caustic potash. It was identified by its burning with a green flame.

The reaction begins in the cold and is accompanied with heat. Cooling the ether in a freezing-mixture does not prevent it. The residual solid was found to be carbonyldiurethane. This renders certain the presence of a third ethoxy group bound to carbon, C—OR, other than the two ethoxy groups in carbonyldiurethane itself, since hydrogen chloride at ordinary temperatures cannot split off alkyl chloride from a nitrogen alkyl derivative,

$$>N{-}C_2H_5,$$

and since carbonyldiurethane is recovered undecomposed. The same decomposition takes place with dilute aqueous hydrochloric acid, slowly in the cold, rapidly on heating. Carbonyldiurethane seems to be the only solid product of the reaction.

Efforts were made to isolate the hydrochloric acid addition product by passing the dry gas into a well-cooled benzene solution of the ether, but with no success. Carbonyldiurethane was alone obtained.



$$\begin{array}{l} NHCOOC_2H_5 \\ | \\ C—OC_2H_5 \\ \| \\ N—COOC_2H_5 \end{array} + HCl \rightarrow \begin{array}{l} NHCOOC_2H_5 \\ | \\ C<^{O\,C_2H_5}_{Cl} \\ | \\ NHCOOC_2H_5 \end{array}$$

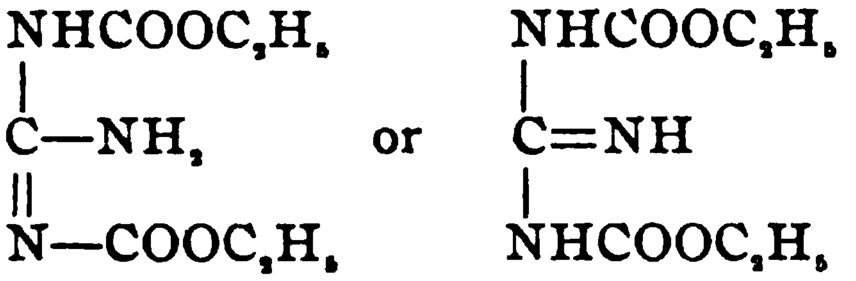
It will be noticed that the stability of the hydrochloric acid addition products decreases with the acidity of the ethers. Thus, while ethyliso-*o*-carbtoluide hydrochloride in a stream of dry hydrogen chloride loses ethyl chloride only at 90°, the more negative ethoxycarbethoxyurea reacts with hydrogen chloride even at 0°.

Action of Alcoholic Ammonia.—The ethoxy ether was dissolved in strong alcoholic ammonia. After a few moments' standing a fine, white precipitate formed. This melted at 163° and proved to be identical with guanidinedicarboxylate obtained by Nenki[1] from guanidine and chlorcarbonic ether. The compound obtained from ethylisodicarbethoxyurea dissolved readily in dilute hydrochloric acid, and with chlorplatinic acid gave a salt which afforded still further proof of its identity.

I. 0.1324 gram substance gave 0.0316 gram platinum.
II. 0.1562 gram substance gave 0.0374 gram platinum.

	Calculated for $C_{14}H_{28}O_8N_6PtCl_6$.	Found. I.	II.
Platinum	23.91	23.87	23.94

Guanidinedicarboxylatechlorplatinate forms hard, red crystals, readily soluble in water. It does not melt at 250°. The formation of this dicarbethoxyguanidine,



$$\begin{array}{l} NHCOOC_2H_5 \\ | \\ C—NH_2 \\ \| \\ N—COOC_2H_5 \end{array} \quad \text{or} \quad \begin{array}{l} NHCOOC_2H_5 \\ | \\ C=NH \\ | \\ NHCOOC_2H_5 \end{array}$$

is of great importance, since it proves definitely that the third

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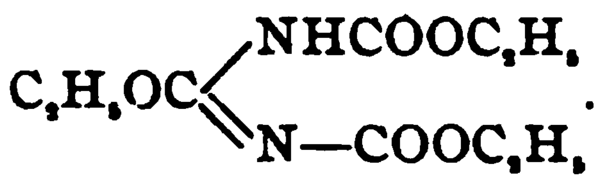
[1] J. *prakt. Chem.* (2), 17, 237.

ethoxy group in ethyl isodicarbethoxyurea is bound to the central carbon atom ; that is, the constitution cannot be

$$\begin{array}{l} \mathrm{C}<^{\mathrm{OR}}_{\mathrm{OR}} \\ \| \\ \mathrm{N{-}CONHCOOR} \end{array}$$

These two reactions, with hydrogen chloride and with ammonia, have shown the presence of an ethoxy group and also its position ; in other words, have definitely proved the constitution of the molecules to be



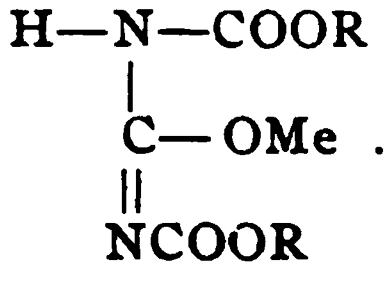
Ethoxycarbonyldiurethane is insoluble in water and in the dilute fixed alkalies, and is not readily decomposed by them. In this respect it bears a close resemblance to the dialphylurea ethers. At the same time, the replacement of an alphyl group by the more negative carbethoxy has increased greatly its reactivity.

The exceeding ease with which ethoxycarbonyldiurethane splits off ethyl chloride with hydrogen chloride, and forms a guanidine derivative with alcoholic ammonia, is in strong contrast to the alphylurea ethers, whose chlorides are relatively stable, and which do not react with alcoholic ammonia below 180°.

As has been pointed out above, this work has a very interesting bearing upon the constitution of the metallic salts of carbonyldiurethane. Since the ethoxydicarbethoxyurea has been shown to have the structure

$$C_2H_5OC(:NCOOR)(NHCOOR),$$

it follows that the silver salt, and hence the other metallic derivatives, must have an analogous constitution, and be represented as follows :



$$\begin{array}{l} \mathrm{H{-}N{-}COOR} \\ \quad\ \ | \\ \quad\ \ \mathrm{C{-}OMe}\ . \\ \quad\ \ \| \\ \quad\ \ \mathrm{NCOOR} \end{array}$$

This structure shows, too, why the ether, though it contains an NH group, is insoluble in alkalies, and why only a monosilver or sodium salt of carbonyldiurethane can be formed.

The investigation of the action of ethyl iodide upon the sodium salt is now being carried on by me. Results already obtained show that when the sodium salt suspended in dry ether is heated with ethyl iodide at 160°, nitrogen, and not oxygen, ethers are formed. Two products were isolated—one an oil which gave a carbylamine reaction and resembles in its properties diethylurethane,

$$C_2H_5NHCOOC_2H_5\,;$$

the other, a solid melting at 91°–92°, insoluble in alkalies, but readily soluble in organic solvents, which also responds to the carbylamine test.

In studying the properties of carbonyldiurethane, the action of ammonia was tried with some interesting results. Carbonyldiurethane was heated with alcoholic ammonia in a sealed tube at 100°, for several hours. The product, on examination, proved to be allophanic ether, showing that saponification had occurred, instead of the normal amide reaction,

$$CO(NHCOOC_2H_5)_2+H_2O \rightarrow NH_2CONHCOOC_2H_5+CO_2+C_2H_5OH.$$

Sodium ethylate, in one case, had the same action.

Different results were obtained when the carbonyldiurethane was heated at 100° with twenty-eight per cent. ammonia. The clear solution, after evaporating off the excess of ammonia, deposited crystals. These heated to 180°–190° partially decomposed with the evolution of a gas, and the formation of a white solid which did not melt on further heating. This same body is obtained by the action of concentrated ammonia in the cold. While the compound was not analyzed, its reactions indicate that it is the ammonium salt of carbonyldiurea,

$$CO(NHCONH_2)_2,$$

which acts like a dibasic acid.

This conclusion is based on the following facts:

a. Its partial decomposition at 190° into a gas and a residual solid.

b. Warming gently with dilute caustic soda gives free ammonia. Carbonyldiurea or biuret is decomposed only with difficulty by caustic alkalies.

c. Dilute acids throw down a precipitate which corresponds in its properties to the carbonyldiurea prepared by Schmidt.[1]

That carbonyldiurea acts as a dibasic acid was shown by the preparation of its silver salt. A solution of the ammonia salt of carbonyldiurea was added to two molecules of silver nitrate. This formed immediately a fine, heavy, white precipitate, which was filtered, washed with dilute ammonia and hot water, and analyzed.

I. 0.2686 gram substance gave 0.1620 gram silver.

II. 0.1958 gram substance gave 0.1182 gram silver.

	Calculated for $C_3O_3H_4N_4Ag_2$.	Found. I.	 II.
Silver..................	60.00	60.31	60.36

The disilver salt is very stable and is discolored only slowly on exposure to the light.

When equal molecules of silver nitrate and carbonyldiurea were mixed no monosilver salt was obtained, but only the disilver compound.

I wish to take this opportunity to thank Prof. Stieglitz for his valuable direction and kindness in the prosecution of this work.

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THE NATURE OF VALENCE.

BY F. P. VENABLE.[2]

Received December 31, 1898.

THE term "valence" is variously defined as the "combining capacity", "capacity of saturation", "quantitative combining power", or "chemical value of the atom." It is well known that the introduction of this idea into chemistry was due to the development of the type theory, a system which had at first a purely empirical basis. Sixty years ago there was still some hesitation as to the acceptance of the atomic theory or the need for such a theory. Much use was made of the term equivalent, which had been Wollaston's expedient for avoiding

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[1] *J. prakt. Chem.* [2], 5, 39.

[2] Address, as chairman, delivered before the North Carolina Section.

the difficulties arising from the full adoption of the theory of atoms.

Wollaston had been himself very far from consistent in the use of the term. The numbers called by him 'equivalent weights' were not infrequently atomic and molecular weights and fully as hypothetical as the so-called atomic weights of Dalton. In the later use of the term it signified solely the numbers obtained by analysis without the introduction of any theoretical considerations. Thus, on analyzing ammonia, the ratio

$$N : H :: 4.6 : 1,$$

is gotten, and therefore the equivalent of nitrogen is 4.6. Strange to say the equivalent given by Wollaston corresponds with the present atomic weight, whereas the atomic weight given by Dalton corresponds with what would be the equivalent.

It is manifest that the idea of equivalents needed something more than the simple theory of atoms to make it clear and tenable. It embodied two distinct conceptions and if we hold to an atomic theory we must introduce a further explanatory theory of the saturation capacity of these atoms. This is the theory of valence or quantivalence or atomicity, and without it the equivalents are purely empirical, and it is most difficult if not impossible to clear up the confusion connected with their use.

Returning now to the derivation of this idea of valence from the type theory, according to Wurtz[1] the conception of valence was introduced into the science in three steps. First there was the discovery of polyatomic compounds. This term was first used by Berzelius in 1827[2], he applying it to such elements as chlorine or fluorine where he thought several atoms of these elements united with a single atom of another element. The term was later applied by Graham, Williamson, and others to compounds.

The second step was the reference of this polyatomicity to what was called the state of saturation of the radicals contained in these compounds. This was largely through the work of Williamson and Gerhardt.

Thirdly this conception of saturation was extended to the elements themselves. This was chiefly due to the work of Frank-

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[1] Histoire des doctrines chimiques, p. 69.

[2] *Jsb. d. Chem.*, 7, 89.

land upon the organo-metallic compounds. And so valence has come to refer to the number of atoms with which a single atom of any element will combine.

This conception has then been one of slow growth, gradually incorporating itself into the science as the necessity arose of devising a suitable explanation for accumulated observations. It was a logical outcome of and was evolved from knowledge acquired step by step. It was no mere speculation or hypothesis, such as that of Prout, evolved by the brilliant fancy or imagination of one man and suddenly appearing with scarcely a claim to foundation upon observed fact.

This conception enters into the chemical theory of to-day almost as fundamentally as the atomic theory itself. Its application is of every-day occurrence and of the most varied character, and yet chemists admit that the nature of valence is one of their chief puzzles and they have advanced but little towards its solution during the past half century. It is quite possible that the ideas to be advanced in the further discussion of this subject in this paper will meet with antagonism. Certainly they should be fully and freely discussed if they are worthy of it. I believe that they form a step toward the clearing up of the mystery of valence.

It is necessary, however, first to trace somewhat further the development of the original conception. One of its earliest and most important applications was to the study of the constitution of the compounds of carbon. Here Kekulé assumed for carbon a constant valence of four, and this idea is still dominant in theories relating to the constitution of these bodies. It was quite natural then that the first belief should have been in a constant valence. It was speedily found, however, that in certain cases, as in the compounds of nitrogen and phosphorus, this belief was scarcely tenable. There were efforts at making it hold good, as, for instance, a distinction was drawn between atomic and molecular compounds, but all of these suggestions have been proved unsatisfactory.

We unquestionably have to account for the existence of a compound with three atoms and another with five atoms in the cases of nitrogen and phosphorus and there are many similar anomalies. Here the valence seems to vary toward one and the same element. Cases might be multiplied to show also that it varies often towards different elements. Thus it frequently happens that the valence of an element towards hydrogen seems to be quite different from that exhibited toward oxygen. For a long time there was much straining to consider the valence of an element always the same but this effort is, in large measure, abandoned now as unavailing and chemists admit that valence is not constant but variable and may even vary towards one and the same element.

The doctrine of valence has had much added to it about bonds, affinities, and linkage, the necessity for which one may well question. Certainly the misuse of the word affinity here, seeing its other and greater use, should be earnestly discountenanced. I am inclined to think that the other terms bring in false and misleading ideas which should be carefully guarded against. At any rate all hypothetical talk about strong bonds, and weak bonds, double bonds and triple is to be avoided.

If then valence varies, can it be an inherent property of the unchanging atoms? Experiments have shown that it varies with the nature of the combining element, that it varies with the temperature and with other conditions. It is not dependent upon the atomic weight in the same sense as other properties are dependent upon it. Thus in the same group the valence remains the same whether the atoms weigh nine times as much as hydrogen or two hundred times as much.

We seem shut up to the conclusion that valence is not one of the primitive inherent properties of the atom but is relative. It is rather to be regarded as the resultant of the mutual influence of the atoms of the combining elements. The clear grasping of this idea is an important step forward. Unfortunately the distinction is not always made nor consistently adhered to.

It may not be amiss to cite here the utterances of Lothar Meyer in regard to the question of a constant or variable valence.[1]

"Since the aim of all scientific investigation is to exhibit the most variable phenomena as dependent upon certain active invariable factors taking part in them and in such a manner that each phenomenon appears to be the necessary result of the properties and reciprocal action of these factors, then it is clear that

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[1] Modern Theories of Chemistry, Eng. Trans., p. 303.

chemical investigation would be considerably advanced were it possible to prove that the composition of chemical compounds is essentially determined by the valency of the atoms and the external conditions under which these atoms react upon one another. The first necessary step in this direction has been made in the attempt to explain the regularities observed in the composition of chemical compounds, by the assumption of a constant power of saturation or an invariable valency of the atom. The opposite and equally hypothetical assumption that the valency is variable leads to no advancement.

"The first step towards progress in this matter would be made if some hypothesis as to the cause of this variability were proposed. This difference between the two attitudes has seldom been properly realized. While some chemists, accepting the the constant valency of atoms, have attempted to deduce the varying atomic linking from one distinct point of view, others have considered it sufficient to have assigned to the atom of a particular element in one compound one valency, and in another compound a different valency, according as this or that value appeared the most suitable, and thus to have given a so-called explanation of the composition of the compounds in question. In this way the fact has been overlooked, that an arbitrary interpretation carried out by means of chosen hypotheses, cannot be regarded as an attempt at a scientific explanation, but is nothing more than an expression of our ignorance of the causal connection of the phenomena. An explanation would require that the different valencies assigned to one and the same element in different compounds, should be traced to a distinct cause. If, for instance, it is stated that carbon in carbon dioxide possesses double the valency which it possesses in carbon monoxide, such a statement is no explanation of the fact that an atom of carbon in the former compound is combined with twice as much oxygen as in the latter, for such a statement is merely a paraphrase which hides its incompetency by assuming the form of an explanation. Although this may be perceived without further remark, still it has frequently occurred during the past few years that similar paraphrases have not only been proposed but also accepted as real explanations of such phenomena. Just as it was formerly supposed that the assumption of a vital force dispensed with a more complete investigation of the phenomena of animal life, so many chemists have of late thought that they possessed in 'variable valency', a means of explaining the varying stoichiometric relationships which would satisfy all claims. Such deceptions can only retard the advance of the science, since they prevent an earnest and thorough investigation of the question, whether each atom is endowed with a property determining and limiting the number of atoms with which it can combine, dependent upon the intrinsic nature of the atom and like it invariable; or whether this ability is variable and with it the nature of the atom itself."

It is not strange that this line of reasoning should lead Lothar Meyer to doubt the unvarying nature of the atom itself, and thus losing his grasp upon one invariable to make sure of another. He says: "It is by no means impossible that the magnitudes which we now style atoms, may be variable in their nature."

It will be an unfortunate day for chemists when the belief in the unchanging atom is given up. Chaos will indeed enter into all of our theories when this, the foundation rock, is left at the mercy of every shifting tide of opinion and can be shaken by all manner of unfounded hypotheses.

The case cannot be so hopeless as to necessitate calling to our aid so dangerous a doctrine. Before turning to such an expedient let us first make all possible use of our atomic theory as it stands. The extension of this theory teaches that the atoms are endowed with motion and this motion probably varies in velocity and phases with the different elements. So too when the atoms unite the resulting molecule has a certain motion peculiar to it while the atoms composing it have an intra-molecular motion in which their original motions are probably modified by their influence upon one another. It is quite manifest then that a molecule, in order to exist, must maintain a certain equilibrium and harmony between these various motions, and that there can be all degrees of equilibrium from the very stable to that which may be upset by the least disturbing influence from without.

It seems to me that herein we have a full and satisfactory means of explaining the various problems connected with the conception of valence. The question as to whether the atoms of two elements will unite is decided by affinity, which is in some way connected with the electrical condition of those atoms. There is no apparent connection between this and valence. The number of atoms which enter into combination forming one molecule is purely a matter of equilibrium and is dependent upon the motion of those atoms. Thus a phosphorus atom unites with chlorine atoms because of a certain affinity between them. The number of chlorine atoms with which it will unite depends upon the possibility of harmonizing the respective motions. As the temperature may affect these motions and also impart a more rapid molecular motion, it is evident that the harmony, or equilibrium, will depend upon the temperature and that a temperature may be reached at which no harmony is possible and hence no compound can be formed. The phosphorus atom mentioned can, as we know, form a stable molecule with five atoms of chlorine. On increasing the temperature this becomes unstable and only three atoms can be retained. Neither with four atoms nor with two is there harmony of motion. A sufficiently high temperature may prevent any harmony of motion whatever being attained and hence union may become impossible.

As to other influences than those of temperature, we can see that the equilibrium between the atom of phosphorus and the five atoms of chlorine may be upset by such a molecule coming within the influence, electrical or vibratory, of a molecule of water. The atoms must rearrange themselves for a new state of equilibrium and so an atom of oxygen takes the place of two atoms of chlorine, giving again a condition of harmony. In other cases the motion of the molecule of water may be of such a character as to directly harmonize with that of the original molecule and so to enter into equilibrium with it, a definite number of such molecules of water affording a condition of maximum stability. This we call water of crystallization. Such molecules would be more or less easily separated by an increase of temperature and where several molecules of water were attached the highest temperature would be necessary for freeing the original molecule from the last water molecule.

A carbon atom finds its most perfect state of equilibrium where four atoms of hydrogen or their equivalents move in harmony with it. But there is a second state of equilibrium where only half that number of atoms are moving with it. This state does not seem to be a possibility where these are hydrogen atoms but is readily possible where the equivalent number of oxygen atoms is concerned. Such a molecule, however, is always in a condition to take up additional atoms until its highest equilibrium is reached and in doing this it proceeds by the regular steps needed for bringing about a harmony of motion. A molecule in a lower state of equilibrium we have become accustomed to call unsaturated, calling that one saturated which is in its highest state of equilibrium. The further application of this hypothesis is easily made and need not be dwelt upon here. It will be helpful in many ways.

This theory of valence makes it clear why it should vary toward the same element under different conditions. It is also clear that it might vary towards different elements as these are very possibly possessed of different motions. It is further evident that it is in accord with the conclusion that valence is not an inherent property of the individual atom but is the resultant of the influence upon each other of the combining atoms.

Only one point remains to be considered: Why do the elements of the same group have practically the same valence? The nearest answer to this, and it seems satisfactory, is that they are all possessed of the same phase or kind of motion. In other words the natural division into periods gives us seven or eight more or less different phases. These are, in large measure, independent of the atomic weight. And so the elements in any given group have the same tendency towards similar states of equilibrium in forming compounds with any other element, as hydrogen or oxygen. Some elements, as copper, mercury, tin, etc., are peculiar in that they may change their phase of motion under certain influences, acting then as if they belonged to different groups and entering into totally different states of equilibrium in forming their compounds.

Lastly it is possible for a combination of atoms of different elements, as NH_4 or CN, to have such molecular and intra-molecular motion that, although not in a state of equilibrium themselves, they are capable of entering into such states just as the single atoms of elements do, having apparently similar valence.

I might develop this theory much further but it is unnecessary [illegible] such an application [illegible] most highly important [illegible] problems springing from [illegible] periodic system.

[illegible] paper require treatment at [illegible] address, it will be fol-[illegible] such portions.

[illegible]

[illegible] OF THE COMMITTEE ON ATOMIC WEIGHTS. RESULTS PUBLISHED IN 1898.

[illegible]

[illegible]

[illegible] been an increased activity [illegible] weights, and a consider-[illegible] published. The [illegible] by the fact that the [illegible] a strong committee to [illegible] weights: and its action for the [illegible] The new data are as follows:

OXYGEN.

[illegible] synthesis of water, by a new [illegible] palladium, the oxygen, [illegible] by successive weigh-[illegible]. For details of construc-[illegible] be consulted. The data [illegible]

[illegible]	[illegible]	[illegible] H – O.	Weight H_2O.
[illegible]	[illegible]	[illegible]	2.45975
[illegible]	[illegible]	[illegible]	2.49923
[illegible]	[illegible]	[illegible]	2.42355
[illegible]	[illegible]	[illegible]	2.40269

From [illegible] second, the ratio H : O can be computed, while the first and [illegible] give the ratio H : H_2O.

Ratio H : O.	Ratio H : H_2O.
7.922	8.929
7.943	8.946
7.939	8.946
7.944	8.950
Mean, 7.937	Mean, 8.943

From ratio H : O, O = 15.874
" " H : H_2O, O = 15.886

Mean, 15.880

[illegible] November, 1898.

This value is very near that obtained by Morley, 15.879; and has corroborative value. Its great merit is in the directness of the determination, and in the avoidance of complicated or troublesome corrections.

NITROGEN.

The equivalent of cyanogen has been determined by Dean;[1] but as yet only an abstract of his work has appeared. Silver cyanide was dissolved in nitric acid, and titrated by Stas' method with potassium bromide. The data give $CN = 26.065$; whence, if $C = 12.01$, $N = 14.055$.

BORON.

Armitage[2] has redetermined the atomic weight of boron by two methods. First, by determination of the percentage of water in borax, which had been washed with alcohol and ether successively, and then dried for six hours in a vacuum. The mean of six experiments gave

$$B = 10.959.$$

Secondly, by the method of Rimbach. Fused borax was dissolved in water and titrated with dilute sulphuric acid. The mean of two experiments gave

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The abstract published gives no details of individual determinations, and neglects to state what values were assigned to the other atomic weights involved in the calculations, except that $O = 16$. The communication was discussed, in the main unfavorably, by Veley, Groves, Scott, and Dewar.

Armitage's paper called forth also a brief note from Leonard,[3] who refers to experiments of his own upon the dehydration of borax. He states that soda and boric acid are both volatilized when borax is intensely ignited, and that the composition of the residue is not constant. From this he concludes that the use of borax for determinations of atomic weight is liable to be attended by serious errors.

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[1] *Chem. News*, 78, 261, November 25, *1898*.

[2] *Ibid.*, 77, 78. A paper read before the Chemical Society. Not yet printed in full.

[3] *Ibid.*, 77, 104.

ZINC.

In the atomic weight determinations made some years ago by Morse and Burton, metallic zinc was converted into oxide, and in that way the ratio between metal and oxygen was measured. Later, Richards and Rogers showed that zinc oxide, prepared as Morse and Burton had prepared it, namely, by conversion of the metal into nitrate and subsequent ignition, always retained occluded gases, and in distinctly weighable quantities.

The research is now completed by the labors of Morse and Arbuckle,[1] who have repeated the determinations made by Morse and Burton, with measurements of the occluded gases, and correction for them. In each experiment the gas, which consisted of oxygen and nitrogen, was analyzed; and the corrections applied assume the liter weights to be, under standard conditions at latitude 45° and sea-level, 1.42923 grams for oxygen, and 1.25461 for nitrogen. The volumes are given in cubic centimeters.

Weight Zn.	Weight ZnO.	Volume gas.	Per cent. O.	Atomic weight Zn.
1.19573	1.48860	0.468	26.28	65.459
1.03381	1.28707	0.402	18.14	65.445
1.06519	1.32599	0.342	18.42	65.459
1.05802	1.31711	0.312	18.58	65.440
1.26618	1.57619	0.521	13.82	65.489
1.03783	1.29198	0.408	35.28	65.475
1.08655	1.35276	0.412	19.55	65.437
1.11364	1.38647	0.456	18.62	65.447
			Mean,	65.457

O = 16. Vacuum weights are given. Without correction for occluded gases, Zn = 65.328, as against the earlier determination of Zn = 65.27. The new determinations agree closely with those of Richards and Rogers, who found Zn = 65.459, and of Richards alone, who found Zn = 65.404. The value assigned to zinc in the table of your committee is 65.41, as published a year ago.

CADMIUM.

In the case of cadmium the same uncertainty existed as in the case of zinc. Morse and Jones had determined the atomic weight by conversion of the metal into the oxide, in that way

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[1] *Am. Chem. J.*, 20, 195, March, *1898*.

finding Cd = 112.06. Morse and Arbuckle[1] have repeated the investigation, this time with search for occluded gases in the oxide, and now give a new series of data, with corrections applied. In all essential features the research is parallel to that upon zinc, which had just been noted; and the results obtained are given in the subjoined table. The weights are reduced to a vacuum, and O = 16.

Weight Cd.	Weight CdO.	Volume of gas.	Per cent. O.	Atomic weight Cd.
1.93188	2.20764	0.574	21.25	112.392
1.67935	1.91910	0.480	25.16	112.365
1.48430	1.69620	0.441	19.95	112.376
1.36486	1.55972	0.402	18.33	112.368
1.50295	1.71744	0.419	21.95	112.394
1.43804	1.64330	0.431	18.56	112.395
1.44041	1.64604	0.406	20.93	112.365
1.45938	1.66771	0.421	21.85	112.375
1.40379	1.60420	0.390	19.50	112.359
			Mean,	112.377

The uncorrected weighings give Cd = 112.084. Bucher, working with cadmium chloride and cadmium bromide, found the mean values 112.39 and 112.38, and the analysis of cadmium sulphate gave 112.36. These results accord fairly well with the determinations made by Dumas and by Huntington, but not with those of Hardin. The weight of evidence, however, now seems to be with the higher value, which may, with much probability, be adopted.

COBALT AND NICKEL.

The paper by Winkler[2] upon these metals is merely a criticism of the determinations by Richards and Baxter, and Richards and Cushman, which were noticed in the committee report for 1897. No new determinations are offered. Winkler suggests that the bromides prepared by Richards and his associates, which were sublimed in porcelain tubes, might have acted upon the glaze of the latter, and so have acquired impurities. He also suggests that perhaps the bromide might have retained an excess of hydrobromic acid, and he points out possible danger in the use of the Gooch crucible, in which the silver bromide was collected.

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[1] *Am. Chem. J.*, 20, 536, July, *1898*.

[2] *Ztschr. anorg. Chem.*, 17, 236, June 25, *1898*.

SELENIUM.

The atomic weight of selenium has been redetermined by Lenher,[1] in the laboratory of the University of Pennsylvania. First, silver selenite was heated in a stream of gaseous hydrochloric acid, giving silver chloride, the latter being quite free from selenium. Three experiments gave as follows :

Weight Ag_2SeO_3.	Weight AgCl.	Atomic weight Se.
0.98992	0.82715	79.326
1.59912	1.33600	79.373
2.70573	2.26087	79.320
		Mean, 79.339

In a second series of eight experiments the silver chloride, after weighing, was reduced to metal in a stream of hydrogen. Thus the ratio between silver selenite and silver was measured. The weighings were as follows :

Weight Ag_2SeO_3.	Weight AgCl.	Weight Ag.
0.26204	0.21897	0.16480
0.58078	0.48522	0.36534
0.70614	0.58999	0.44417
0.80811	0.67532	0.50821
0.98396	0.82232	0.61882
1.29685	1.08350	0.81562
1.63103	1.36288	1.02588
2.00162	1.67234	1.25884

Hence, for the atomic weight of selenium we have :

Ag_2SeO_3 : AgCl.	As_2SeO_3 : Ag.
79.299	79.356
79.371	79.280
79.350	79.301
79.282	79.369
79.263	79.358
79.361	79.277
79.316	79.320
79.358	79.357
Mean, 79.325	Mean, 79.329

Still another set of determinations was based upon analyses of ammonium bromoselenate, Am_2SeBr_6. This salt was reduced by hydroxylamine hydrochloride, and the precipitated selenium was weighed in a Gooch crucible. The results are subjoined:

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[1] This Journal, 20, 555, August, *1898*.

Weight Am_2SeBr_6.	Weight Se.	Atomic weight Se.
1.00059	0.13324	79.243
1.50153	0.20022	79.367
2.00059	0.26649	79.273
2.00126	0.26657	79.269
3.00125	0.39958	79.226
4.00216	0.53346	79.333
5.00218	0.66656	79.306
5.03001	0.66998	79.267
	Mean,	79.285

General mean of all twenty-seven determinations,

$$Se = 79.314.$$

The antecedent values are O = 16, H = 1.008, N = 14.04, Ag = 107.92, Br = 79.95, Cl = 35.45. All weights were reduced to a vacuum.

The result obtained is near that found by Dumas, but considerably higher than that given by Ekman and Pettersson. The reason for this disaccordance is yet to be found. In the table at the end of this paper the value assigned to selenium is the mean of Lenher's determination, and the value given in the report of last year; namely, when O = 16,

$$Se = 79.17.$$

Neither the new nor the old determinations can be yet adopted to the exclusion of the other, and the mean value is the safest for present use.

TELLURIUM.

Metzner[1] has employed two methods for determining the atomic weight of this element. First, by synthesis of the sulphate, Te_2SO_7, which is perfectly stable at 440°. The tellurium which served as the starting-point was prepared by dissociation of hydrogen telluride, and was crystallized in beautiful needles. By solution in sulphuric acid, evaporation to dryness, and calcination at temperatures not over 440°, the sulphate was produced. The weights given are probably milligrams.

Weight Te.	Weight sulphate.	Atomic weight Te.
790.2	1235.0	127.9
414.3	647.5	128.0
1098.3	1717.0	127.8

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[1] *Ann. chim. phys.* [7], 15, 272, October, 1898.

Metzner's second method consisted in reducing tellurium dioxide by carbon monoxide, in presence of metallic silver. The latter prevents the volatilization of tellurium.

Weight TeO_2	Loss of weight.	Atomic weight Te.
743.2	118.8	127.8
1106.7	221.3	128.0
988.5	197.0	128.24
1312.5	263.0	127.75

Metzner adopts 127.9 as the final result of his investigation. Apparently his weights were not reduced to a vacuum, and he neglects to state what value he assumed for the atomic weight of sulphur. O = 16 was evidently the basis of his calculations.

The work of Metzner called forth two theoretical papers by Wilde,[1] who holds that the experiments show that the true value for tellurium is 128. In his second paper he discusses the positions of tellurium and iodine in the periodic system. As both communications are purely critical in character, and contain no new data, they need no further notice here.

Still another set of determinations relative to tellurium is due to Heberlein.[2] First, telluric acid was dissolved in hydrochloric acid, and the liberated chlorine was distilled off into a dilute solution of potassium iodide. In the latter, iodine was set free, and was titrated with a decinormal solution of sodium thiosulphate. The values found for Te, with O = 16 and H = 1.008 are

127.16
127.28
127.32
127.35
127.09
Mean, 127.24

Secondly, telluric acid was transformed into tellurium dioxide, by heating with proper precautions to avoid loss.

Weight $H_2TeO_4.2H_2O$.	Loss of weight.	Atomic weight Te.
1.35236	0.41431	126.60
1.76859	0.54122	126.84
		Mean, 126.72

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[1] *Compt. rend.*, 127, 613, 616.

[2] Beitrage zur Kenntnis des Tellur's.—Doctoral Dissertation: Strassburg, 1898.

Thirdly, tellurium dioxide was reduced to tellurium by means of hydrogen, in presence of metallic silver.

Weight TeO_2.	Loss of weight.	Atomic weight Te.
1.35908	0.37353	126.99
1.94038	0.39050	127.00
	Mean,	126.995

The mean of all three series is Te = 126.985.

It will be seen that some of these values range below, and others above, the atomic weight of iodine. Heberlein regards the higher figures as too high, and the lower as probably too low, the mean of all being most nearly correct. The main question, the position of tellurium in the periodic system, he considers experimentally unsettled, but favors the opinion that more critical determinations will place it below iodine and in the sulphur-selenium group. The value which he has actually found is only a trifle higher than that of iodine, and better determinations may well reduce it to the necessary amount.

ZIRCONIUM.

Venable[1], in order to determine the atomic weight of this element, has availed himself of the oxychloride, $ZrOCl_2.3H_2O$. This compound can be crystallized from strong hydrochloric acid, and dried in a current of gaseous hydrochloric acid at 100°–125° without loss of its water. When dissolved in water in a platinum crucible, evaporated to dryness, and strongly ignited, pure zirconia, free from chlorine, remains. The ratio $ZrOCl_2.3H_2O : ZrO_2$ is thus determined, and from it the atomic weight of the metal is calculable. The results of ten experiments are given by Venable, as follows:

Weight $ZrOCl_2.3H_2O$.	Weight ZrO_2.	Ratio.
5.25762	2.78450	52.961
3.53994	1.87550	52.981
3.25036	1.72435	53.051
1.52245	0.80708	53.012
1.98802	1.58274	52.969
2.11371	1.11920	52.949
2.38139	1.26161	52.978
1.90285	1.00958	53.055
2.61847	1.38658	52.954
1.07347	0.56840	52.951
26.64828	14.11953	52.986

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[1] This Journal, 20, 119, February, 1898.

Hence, if $O = 16$, $H = 1.008$, and $Cl = 35.45$, the atomic weight of zirconium becomes

90.78 in mean,
91.12 maximum,
90.61 minimum.

As further results are promised, this investigation is to be regarded as a preliminary research, rather than as a final determination.

THORIUM.

Brauner's work upon the atomic weight of thorium[1] has as yet appeared only in abstract. The determinations were made with the normal oxalate, in which thorium dioxide was estimated by heating, and the C_2O_3 was measured by titration with potassium permanganate. The values found for thorium with $O = 16$, were

232.50	232.33
232.46	232.50
232.45	232.44
232.31	232.35

In mean, Th = 232.42.

CERIUM.

Brauner's paper upon the compound nature of cerium,[2] has also only appeared in abstract. By a series of fractionations oxides were obtained giving atomic weights ranging from 140.25 down to 130.70. As the atomic weight decreases, the color of the oxide changes from white to reddish-brown orange. Brauner infers that cerium is accompanied by another metal of atomic weight about 110. Yttrium was looked for in the lower fractions, but not found, nor were there any lines in the spark spectra, other than those of cerium. The supposed new element, like gadolinium, may have no characteristic spectrum.

THE DIDYMIUMS.

Jones[3] has determined the atomic weights of neodymium and praseodymium by means of the synthesis of the sulphates from the oxides. The material for the investigation was furnished by Wal-

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[1] *Chem. News*, 77, 160, April 7, *1898*.

[2] *Ibid.*, 77, 160, April 7, *1898*.

[3] *Am. Chem. J.*, 20, 345, May, *1898*.

dron Shapleigh, and was very nearly pure. It was further purified by repeated fractional crystallizations of the double ammonium nitrates. From these salts the oxalates were prepared, and, from the latter, the oxides. The superoxide of praseodymium, Pr_4O_7, was reduced to Pr_2O_3 by ignition in hydrogen.

For praseodymium the results obtained were as follows, when O = 16 and S = 32.07:

Weight Pr_2O_3.	Weight $Pr_2(SO_4)_3$.	Atomic weight Pr.
0.5250	0.9085	140.42
0.6436	1.1135	140.50
0.7967	1.3788	140.38
0.7522	1.3018	140.38
0.7788	1.3473	140.53
0.6458	1.1172	140.54
0.6972	1.2062	140.51
0.7204	1.2464	140.49
0.8665	1.4990	140.54
0.6717	1.1624	140.40
0.7439	1.2873	140.42
0.6487	1.1224	140.47
8.4905	14.6908	140.46

With O = 15.88, Pr = 139.41.

For neodymium the data are as follows:

Weight Nd_2O_3.	Weight $Nd_2(SO_4)_3$.	Atomic weight Nd.
0.8910	1.5296	143.58
0.7880	1.3530	143.51
0.9034	1.5509	143.57
0.7668	1.3166	143.51
0.8908	1.5296	143.49
0.8848	1.5194	143.46
0.8681	1.4903	143.57
0.8216	1.4103	143.62
0.8531	1.4646	143.56
0.8711	1.4957	143.50
0.8932	1.5332	143.62
0.8893	1.5268	143.55
10.3212	17.7200	143.55

This value for neodymium must be corrected for the presence of a little praseodymium, which was estimated by the intensity of its lines in the spectrum. Corrected it becomes 143.6, or 142.52 when O = 15.88.

now. Enough has been said to show that such an application of the atomic theory is legitimate and is most highly important as a step towards the clearing up of the problems springing from the conception of valence and from the periodic system.

Note.—Since certain points in this paper require treatment at greater length than was practicable in an address, it will be followed by a second paper elaborating such portions.

UNIVERSITY OF NORTH CAROLINA, December 29, 1898.

SIXTH ANNUAL REPORT OF THE COMMITTEE ON ATOMIC WEIGHTS. RESULTS PUBLISHED IN 1898.

BY F. W. CLARKE.

Received January 10, 1898.

DURING the year 1898, there has been an increased activity in the determination of atomic weights, and a considerable number of investigations have been published. The importance of the subject is also indicated by the fact that the German Chemical Society has appointed a strong committee to report annually upon atomic weights; and its action for the current year is stated farther on. The new data are as follows:

OXYGEN.

Keiser[1] has effected the complete synthesis of water, by a new method, in which the hydrogen held by palladium, the oxygen, and the water produced are all determined by successive weighings in one and the same apparatus. For details of construction, etc., the original memoir must be consulted. The data for four experiments are as follows:

Weight H.	Weight O.	Sum H + O.	Weight H_2O.
0.27549	2.18249	2.45798	2.45975
0.27936	2.21896	2.49832	2.49923
0.27091	2.15077	2.42168	2.42355
0.26845	2.13270	2.40115	2.40269

From columns first and second, the ratio H : O can be computed, while the first and fourth give the ratio H : H_2O.

	Ratio H : O.		Ratio H : H_2O.
	7.922		8.929
	7.943		8.946
	7.939		8.946
	7.944		8.950
Mean,	7.937	Mean,	8.943

From ratio H : O, O = 15.874
" " H : H_2O, O = 15.886

Mean, 15.880

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[1] *Am. Chem. J.*, 20, 733, November, *1898*.

This value is very near that obtained by Morley, 15.879; and has corroborative value. Its great merit is in the directness of the determination, and in the avoidance of complicated or troublesome corrections.

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[1] *Chem. News*, 78, 261, November 25, *1898*.

[2] *Ibid.*, 77, 78. A paper read before the Chemical Society. Not yet printed in full.

[3] *Ibid.*, 77, 104.

Li,	7.0	I,	126.23	Cu,	63.339
Na,	23.06	N,	14.0	Ag,	107.717
K,	39.111	O,	16.0	Au,	195.77
Rb,	84.96	F,	18.928	Hg,	198.45
Cs,	131.1	B	11.041	Zn,	65.385
Cl,	35.464	C,	11.9497	Cd,	112.0
Br,	79.666	Si,	28.0	Tl,	204.298

NEW TABLES.

Two new tables of atomic weights have appeared during the year; one by Richards,[1] the other by a committee of the German Chemical Society, consisting of Professors Landolt, Ostwald, and Seubert.[2] Both tables coincide in the main with that of your committee, but in some instances there are differences which can be eliminated only by new investigations.

Richards' table is preceded by a careful discussion of some points at issue, especially as regards the atomic weights of antimony, cadmium, calcium, magnesium, platinum, tungsten and uranium. For antimony, Richards prefers the value 119.92, or in round numbers 120, which depends on Cooke's analyses of the bromide, and involves the rejection of other data which seem entitled to some weight. For cadmium he accepts the higher value 112.3, rather than 112. Morse and Arbuckle's recent work lead me to adopt the value 112.38 for the present, bringing the committee table into harmony with that of Richards. In the case of calcium Richards regards the value 40.07 as too high, and adopts the round number 40. For magnesium, two values are in controversy, and here again Richards accepts the higher. In this case more evidence is needed. The same thing is true of platinum, tungsten, and uranium. The atomic weights of all three are uncertain to some tenths of a unit at least, and where Richards has selected data, I have preferred to use least square averages. New and better determinations are necessary in all three cases.

The committee of the German Chemical Society present their table without discussion of the data, so that it represents their careful judgment as to the best values for analytical use, unencumbered by argument. All three of the members, however, argue at length in favor of O = 16, as the basis of the scale, and give the well-known reasons in support of that view. Apart

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[1] *Am. Chem. J.*, 20, 543, July, *1898*.

[2] *Ber. d. chem. Ges.*, 31, 2761, November 28, *1898*.

from theory, the oxygen scale certainly has the merit of greater convenience. The committee also suggest the desirability of an international commission upon atomic weights, and in that all chemists are likely to agree.

In the following table of atomic weight your committee give first its own sets of values, based upon both standards, H = 1, and O = 16. These values are only rounded off to the second decimal place, and represent, so far, the actual results of recalculation from the original data. Next is given Richards' table, and finally the table of the German Chemical Society, both sets of constants being more or less rounded off by the authors for convenience in practical use. It will be seen at once that the values adopted are in most cases sensibly identical. The new elements coronium, polonium, radium, monium, etherion, krypton, neon, xenon, and metargon are omitted, for lack of sufficiently precise data.

	Clarke.			
	H = 1.	O = 16.	Richards.	German.
Aluminum	26.91	27.11	27.1	27.1
Antimony	119.52	120.43	120.0	120.
Argon	?	?	39.9	40.
Arsenic	74.44	75.01	75.0	75.
Barium	136.39	137.43	137.43	137.4
Bismuth	206.54	208.11	208.0	208.5
Boron	10.86	10.95	10.95	11.
Bromine	79.34	79.95	79.955	79.96
Cadmium	111.54	112.38	112.3	112.
Caesium	131.89	132.89	132.9	133.
Calcium	39.76	40.07	40.0	40.
Carbon	11.91	12.00	12.001	12.00
Cerium	138.30	139.35	140.0	140.
Chlorine	35.18	35.45	35.455	35.45
Chromium	51.74	52.14	52.14	52.1
Cobalt	58.55	58.99	59.00	59.
Columbium	93.02	93.73	94.0	94.
Copper	63.12	63.60	63.60	63.6
Erbium	165.06	166.32	166.0	166.
Fluorine	18.91	19.06	19.05	19.
Gadolinium	155.57	156.76	156.0	....
Gallium	69.38	69.91	70.0	70.
Germanium	71.93	72.48	72.5	72.
Glucinum	9.01	9.08	9.1	9.1
Gold	195.74	197.23	197.3	197.2
Helium	?	?	4.0	4.
Hydrogen	1.000	1.008	1.0075	1.01

	Clarke.			
	R = 1.	O = 16.	Richards.	German.
Indium	112.99	113.85	114.0	114.
Iodine	125.89	126.85	126.85	126.85
Iridium	191.66	193.12	193.0	193.
Iron	55.60	56.02	56.0	56.
Lanthanum	137.59	138.64	138.5	138.
Lead	205.36	206.92	206.92	206.9
Lithium	6.97	7.03	7.03	7.03
Magnesium	24.10	24.28	24.36	24.36
Manganese	54.57	54.99	55.02	55.
Mercury	198.49	200.00	200.0	200.3
Molybdenum	95.26	95.99	96.0	96.
Neodymium	142.52	143.60	143.6	144.
Nickel	58.24	58.69	58.70	58.7
Nitrogen	13.93	14.04	14.045	14.04
Osmium	189.55	190.99	190.8	191.
Oxygen	15.88	16.00	16.000	16.00
Palladium	105.56	106.36	106.5	106.
Phosphorus	30.79	31.02	31.0	31.
Platinum	193.41	194.89	195.2	194.8
Potassium	38.82	39.11	39.140	39.15
Praseodymium	139.41	140.46	140.5	140.
Rhodium	102.23	103.01	103.0	103.0
Rubidium	84.78	85.43	85.44	85.4
Ruthenium	100.91	101.68	101.7	101.7
Samarium	149.13	150.26	150.0	150.
Scandium	43.78	44.12	44.0	44.1
Selenium	78.58	79.17	79.0	79.1
Silicon	28.18	28.40	28.4	28.4
Silver	107.11	107.92	107.93	107.93
Sodium	22.88	23.05	23.050	23.05
Strontium	86.95	87.61	87.68	87.6
Sulphur	31.83	32.07	32.065	32.06
Tantalum	181.45	182.84	183.0	183.
Tellurium	126.52	127.49	127.5	127.
Terbium	158.80	160.00	160.0	....
Thallium	202.61	204.15	204.15	204.1
Thorium	230.87	232.63	233.0	232.
Thulium	169.40	170.70	170.0	....
Tin	118.15	119.05	119.0	118.5
Titanium	47.79	48.15	48.16	48.1
Tungsten	183.43	184.83	184.4	184.
Uranium	237.77	239.59	240.0	239.5
Vanadium	50.99	51.38	51.4	51.2
Ytterbium	171.88	173.19	173.0	173.
Yttrium	88.35	89.02	89.0	89.
Zinc	64.91	65.41	65.40	65.4
Zirconium	89.72	90.40	90.5	90.6

NOTE.

Drown's Method of Determining Silicon.[1]—In the July number of this Journal, George Auchy has described a method devised by him, which will effect a more thorough dehydration of the silica than is obtained by the method usually followed. Dr. Dudley[2] called attention to the difficulty of dehydrating in this case at the Troy meeting of this society in 1896.

Without claiming any superiority over Mr. Auchy's method it may be of interest to describe a modification which has been in use in this laboratory for a number of years. It is not original with the author.

The pig iron or steel is weighed into a No. 4 beaker and brought into solution by the usual method as described by Blair. We then add forty cc. of concentrated sulphuric acid and evaporate to fumes on the hot plate. A leather strap about one inch broad and twenty inches long is passed under the lip of the beaker and the ends clasped between the thumb and forefinger. By a slight wrist movement the contents of the beaker are given a rapid rotary movement. The beaker can, in this way, be heated directly in the full flame of the Bunsen burner with perfect safety. Care only must be taken that the contents are kept in continual motion and that sufficient acid is present to cover the glass exposed to the flame. Under these circumstances any lumps are broken up and a thorough contact between the silica and the very hot acid is insured. In many other cases where evaporation to fumes is necessary and the tendency to bump prevents the simple boiling down of the solution, the use of a strap in this way is invaluable. As a rule, it will be found more convenient than the use of the casserole. It is also very convenient in handling hot beakers as it is adaptable to one of any size.

We perhaps run the risk of recounting what may be to some chemists an old story, but, as in our experience we have yet to visit a laboratory in which the strap was used in this way, it is but reasonable to conclude that it has not met with the attention it deserves.

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NEW YORK.

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[1] This Journal, 20, 547.

[2] *Ibid.*, 19, 106.

BOOKS RECEIVED.

Commercial Organic Analysis. A treatise on the properties, proximate analytical examination, and modes of assaying the various organic chemicals and products employed in the arts, manufactures, medicines, with concise methods for the detection and determination of their impurities, adulterations, and products of decomposition. By Alfred H. Allen, F.S.C., F.C.S. Third Edition, Illustrated. With revisions and addenda by the author and Henry Leffmann, M.A., M.D. Volume II.—Part I.—Fixed Oils, Fats, Waxes, Glycerol, Nitroglycerin and Nitroglycerin Explosives. Philadelphia: P. Blakiston's Son & Co. 1899. x+371 pp. Price, $3.50.

Fish as Food. By C. F. Langworthy, Ph.D. Farmer's Bulletin, No. 85, U. S. Department of Agriculture, Washington, D. C. 1898. 30 pp.

Grasses, Clovers, Forage, and Economic Crops. By W. R. Dodson and Wm. C. Stubbs. Bulletin No. 53, Second Series, of the Agricultural Experiment Station of Louisiana State University and A. and M. College, Baton Rouge, La. 55 pp. and several plates.

Vinegar Adulteration and the Extent to Which It Exists in the Samples for Sale in North Carolina. Bulletin No. 153, The North Carolina Agricultural Experiment Station, Raleigh, N. C. 8 pp.

The Adulteration of Coffee and Tea Offered for Sale in North Carolina. Bulletin No. 154, The North Carolina Agricultural Experiment Station, Raleigh, N. C. 16 pp.

Electrolysis and Electrosynthesis of Organic Compounds. By Dr. Walther Löb. Authorized Translation by H. W. F. Lorenz, A.M., Ph.D. New York: John Wiley & Sons. 1898. xiii+103 pp. Price, $1.00.

Ninth Annual Report of the Kentucky Agricultural Experiment Station of the State College of Kentucky for the Year 1896, containing also Bulletin No. 61 (Potatoes), Bulletin No. 62 (Strawberries), Bulletin No. 63 (Tobacco), Bulletin No. 64 (Analyses of Commercial Fertilizers), and Bulletin No. 65 (Analyses of Commercial Fertilizers). Kentucky Agricultural Experiment Station, Lexington, Ky. 1898. xliii+114 pp.

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Lavas and Soils of the Hawaiian Islands. Investigations of the Hawaiian Experiment Station and Laboratories. Walter Maxwell, Director and Chief Chemist. Honolulu: The Hawaiian Sugar Planters' Association. 1898. 186 pp.

Text-book of Medical and Pharmaceutical Chemistry. By Elias H. Bartley, B.S., M.D., Ph.G. Fifth Edition, Revised and Enlarged. Philadelphia: P. Blakiston's Son & Co. 1898. xiv+738 pp., with 96 illustrations. Price, $3.00

VOL. XXI. [MARCH, 1899.] NO. 3.

THE JOURNAL

OF THE

AMERICAN CHEMICAL SOCIETY.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY.]

THE SOLUBILITY OF IODINE IN DILUTE POTASSIUM IODIDE SOLUTIONS.[1]

BY A. A. NOYES AND L. J. SEIDENSTICKER.

Received October 12, 1898.

FROM the investigation of Jakowkin[2] on the distribution of iodine between carbon disulphide and tolerably dilute potassium iodide solutions, it would seem almost beyond doubt that the iodine in these solutions is present chiefly in the form of the compound KI_3. This assumption, however, is apparently in contradiction with the well-known fact, which has been quantitatively confirmed by the experiments of Dossios and Weith,[3] that from a strong solution of potassium iodide which has been saturated with iodine, the iodine is, for the most part, precipitated by dilution with water, for the following equation of equilibrium must evidently hold true:

$$KI_3 = k\,(KI) \times (I_2)$$

where the symbols represent the concentrations of the substances, and k is a constant. If now the solutions are kept saturated

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[1] Read at the Boston meeting of the American Chemical Society, August 25, 1898.

[2] *Ztschr. phys. Chem.*, 13, 539; 20, 19.

[3] *Ztschr. Chem.*, 1869, 379.

with iodine, then its concentration is constant, and the above equation becomes

$$(KI_3) = k\,(KI).$$

That is, the concentration of the periodide is directly proportional to that of the iodide, and dilution should bring about no separation of iodine. It seemed now not improbable that this apparent contradiction between the results of Jakowkin and those of Dossios and Weith could be explained by the fact that the former results have reference to fairly dilute, and the latter to concentrated solutions. The purpose of this investigation was to test this explanation, and at the same time to establish the application of the law of mass action in such a case; namely, a case where a salt solution is saturated with a substance which forms with the salt a simple chemical compound. To this end, we have determined the solubility of iodine in potassium iodide solution between the concentrations of 0.1 and 0.0008 normal, as well as in pure water.

The requisite potassium iodide was obtained by twice recrystallizing a commercial preparation, and the iodine was prepared by sublimation from a mixture of it with potassium iodide. Two solutions of known strength, about 0.1 and 0.0067 normal, were prepared by weighing out the salt, and from these six others were obtained by dilution. To four portions of these solutions of each concentration, there was added an excess of finely divided iodine; and the mixtures were then rotated in bottles with glass stoppers in a thermostat at 25°, by means of the earlier described apparatus.[1] Duplicate determinations were always made in such a way that the state of saturation was approached both from a higher and from a lower temperature. Furthermore, each pair of determinations was checked by a second, in which fresh solutions prepared by weighing out the iodide anew were used. After the bottles had been rotated from four to five hours, the solutions were allowed to stand over night to settle; twenty-five or fifty cc. were then pipetted out, and the dissolved iodine was titrated by means of sodium thiosulphate with starch as an indicator. In determining the solubility in water, particular regard was paid to the purity of the water, which was distilled from alkaline permanganate, and proved pure by measur-

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[1] *Ztschr. phys. Chem.*, 9, 606.

ing its conductivity. In order to detect any slight influence due to the formation of hydriodic acid, the bottles were rotated in the thermostat during different lengths of time; but no difference in the results could be detected.

The following table contains the results in millimols, or thousandths of a molecular weight, per liter. Under the heading "undersaturated", the values are given which were obtained by warming from a lower temperature up to 25°, while under "supersaturated", those appear which were obtained in the opposite way.

SOLUBILITY OF IODINE.

Millimols of KI per liter.	Millimols of dissolved iodine (I_2) per liter.				
	Undersaturated.		Supersaturated.		
	I.	II.	III.	IV.	Mean.
106.3	55.20	55.39	55.14	55.38	55.28 ±0.05
53.15	28.03	27.97	28.16	27.96	28.03 ±0.03
26.57	14.70	14.65	14.72	....	14.68 ±0.02
13.29	8.018	7.992	7.998	8.003	8.003±0.004
6.643	4.678	4.712	4.589	4.688	4.667±0.019
3.322	3.138	3.061	2.906	3.102	3.052±0.036
1.661	2.223	2.214	2.241	2.262	2.235±0.008
0.8304	1.830	1.838	1.779	1.809	1.814±0.010
0	1.363	1.347	1.465[1]	1.283[1]	1.342±0.004[2]
0	1.302	1.337	1.341	1.357	
0	1.333	....	1.329	1.351	
0	1.343	....	1.360	....	

An inspection of the table shows that no regular difference exists between the "undersaturated" and the "supersaturated" values, which proves that the solutions had reached the state of equilibrium. The degree of concordance of the single results is best shown by the values of the deviations from the mean in the last column. From the results with pure water, it is obvious that the amount dissolved was independent of the time during which the bottles were rotated. The solubility found (1.342 millimols) agrees also well with that obtained by Jakowkin (0.3387 gram or 1.335 millimols per liter).

In order now to test the application of the law of mass action, we must first of all subtract from the total amount of dissolved

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[1] Omitted in the calculation of the mean.

[2] In determining the amount of iodine necessary to saturate pure water, the bottles were rotated during different lengths of time; namely, as follows: first series, two hours; second series, four hours; third series, one day; fourth series, seven days.

iodine, the amount of iodine soluble in pure water. In this way, the amount of iodine is found which is present in the form of the complex salt; and, if the ratio of this quantity to the total amount of potassium iodide is calculated, it can be seen at once to what extent the simple proportionality exists which the law of mass action requires in case only the compound KI_3 is formed. The results (expressed in millimols) of this calculation are arranged in the following table:

$KI+KI_3$.	$KI+I_2$.	KI_3.	Ratio. $KI_3 : (KI+KI_3)$.
106.3	55.28	53.94	0.5074
53.15	28.03	26.69	0.5021
26.57	14.68	13.34	0.5021
13.29	8.003	6.661	0.5012
6.643	4.667	3.325	0.5005
3.322	3.052	1.710	0.5148
1.661	2.235	0.893	0.5376
0.8304	1.814	0.472	0.5684

It is evident from the last column of this table that between the concentrations 0.1 and 0.006 normal the iodine present in the form of a complex salt is closely proportional to the total quantity of potassium iodide. In the case of the more dilute solutions, however, the relation of these two quantities seems to increase; but this is probably to be attributed to experimental error, for the quantity of iodine present as complex salt is less in these cases even than the solubility in pure water. Aside from these very dilute solutions, the assumption that the iodine exists exclusively as free iodine and as a constituent of the salt KI_3 (or of its anion) is therefore in complete accord with the law of mass action. The conclusion of Jakowkin in regard to the constitution of the complex salt is thus confirmed by the solubility relations.

THE NATURE OF VALENCE.

[SECOND PAPER.]

BY F. P. VENABLE.

Received January 23, 1899

As the preceding paper upon this subject was in the form of an address before one of the local sections of the society, the hypothesis as to the cause of valence there suggested was given in outline only and could not be enlarged upon as far as may have been necessary. In the present paper it is proposed to elaborate certain points and to test, as far as possible, the reasonable nature of the hypothesis.

While the whole subject of valence has been much confused, and the use of some of the terms connected with it unfortunate, no part of it has given greater trouble than its variability. This is the very point, however, which affords the best clew to its solution and should therefore be treated at some length.

The most instructive cases of varying valence are those where the variation is shown towards the same element, as in the compounds PCl_3 and PCl_5, $FeCl_2$ and $FeCl_3$, Hg_2O and HgO, CO and CO_2, and many other similar compounds. There are two possible views regarding these. Either the valence varies or the valence remains the same and the differences are explained by some such assumption as that of a state of saturation of the atom and of various unsaturated states.

The terms 'saturated' and 'unsaturated' present a number of anomalies as commonly used. In the first place the term saturated is not always used for that condition of the atom in which it is united with the largest number of other atoms. Thus, ferrous oxide (FeO) is called unsaturated, and ferric oxide (Fe_2O_3) saturated, though there is a larger proportion still of oxygen in ferric acid and the ferrates. The same is true of the three series of manganese and chromium compounds.

Again the term saturated does not carry with it any definite relation to the stability of the compound. Sometimes the compound called unsaturated, and containing the least number of atoms is the most stable, sometimes that with the largest number. Phosphorus trichloride is more stable than the pentachloride, but the pentoxide is more stable than the trioxide. The most stable of the manganese compounds are the so-called unsaturated manganous salts; in the case of chromium it would appear to be the chromic salts. In the case of carbon the saturated compounds are the most stable. It is manifest that these two terms cannot cover all cases of combination for a number of elements. It would seem wiser and simpler then to speak of the valence directly when discussing the elements, as bivalent carbon or quadrivalent carbon; bivalent or trivalent iron, etc. In the case of carbon compounds the terms have acquired a somewhat different meaning and are too thoroughly incorporated in the literature for a change to be suggested. Saturated here means a compound which can take on no further atoms by addition, while an unsaturated compound can have such atoms added.

Certain cases of change of valence, as in cuprous and cupric compounds, mercurous and mercuric, ferrous and ferric, etc., have been looked upon as presenting some peculiar relationships. Such cases are spoken of by some as if they occurred among positive elements only. It is not clear how any distinction can be drawn between these and the classes phosphorous and phosphoric, sulphurous and sulphuric, nitrous and nitric, chlorous and chloric, etc. A possible distinction might be made that the more negative the element the greater the number of changes of valence; the more positive the element the less variation in valence is observed. This would be an approximation only.

So great is the difference caused by this variation in the valence that some have even thought it best to arrange what have been called the lower and higher stages under different groups. Thus Mendeléeff placed cuprous copper in Group I, and cupric copper in Group VIII; aurous gold in Group I and auric gold in Group VIII. Such an arrangement would, however, greatly confuse the periodic system. Mercury, thallium, chromium, manganese, phosphorus, arsenic, sulphur, selenium, and others would have to be similarly provided for. It is better to retain them in the positions to which their atomic weights would assign them and to study them more thoroughly, so that we may understand why certain elements, as copper, gold, and mercury show this peculiarity while others closely akin to them, as silver, zinc, and cadmium, do not. In studying the nature of valence from the standpoint of its variability, the means by which these variations can be brought about must have an important bearing upon the subject. There are a number of these agencies.

Light.—It is a matter of common observation that light can bring about physical, and the most varied chemical, transformations. In some cases it is apparent that the transformation is one from a higher to a lower valence or *vice versa*. Thus, certain mercurous compounds can be changed to mercuric.

$$Hg_2O = HgO + Hg.$$

An alcoholic solution of ferric chloride is changed by light to ferrous chloride.

$$2FeCl_3 + C_2H_6O = 2FeCl_2 + C_2H_4O + 2HCl.$$

Ferric oxalate under the influence of light gives off carbon dioxide and becomes ferrous oxalate.

$$Fe_2(C_2O_4)_3 = 2Fe(C_2O_4) + 2CO_2.$$

An alcoholic solution of cupric chloride becomes cuprous chloride. Mercuric chloride in aqueous solution is slowly changed to mercurous when exposed to the light.

$$2HgCl_2 + H_2O = 2HgCl + 2HCl + O.$$

Gold chloride ($AuCl_3$), in contact with organic substances, when exposed to light, is changed first to aurous chloride ($AuCl$) and then to metallic gold.

It is quite well known that a ray of light falling upon a piece of selenium changes its conducting power for electricity. This is not a change of valence but has, it would seem, its bearing upon the problem as a possible change in vibration. The chemical action of light is generally attributed to the vibrations set up among the molecules. Rays having the shortest wave-lengths and the greatest frequency are most active in this respect though all the rays of the visible spectrum have been shown to exert some action. So far as this variation in valence is caused by light then the hypothesis of a change in vibration necessitating a change in equilibrium may well serve as an explanation.

Heat.—Again these variations are often easily brought about by changes of temperature. Thus cupric chloride becomes cuprous chloride.

$$CuCl_2 = CuCl + Cl.$$

Mercurous chloride is temporarily changed into mercuric, the mercurous re-forming upon cooling.

$$2HgCl = Hg + HgCl_2.$$

Phosphorus pentachloride becomes the trichloride.

$$PCl_5 = PCl_3 + Cl_2.$$

Arsenic pentoxide becomes trioxide.

$$As_2O_5 = As_2O_3 + O_2.$$

An interesting series of changes are those in the sulphur chlorides. Thus sulphur tetrachloride (SCl_4) becomes sulphur dichloride (SCl_2), if warmed above —22°, and this becomes sulphur monochloride (S_2Cl_2), if heated above 64°. This last can be boiled without change.

These instances might be multiplied but it is not necessary. The most plausible explanation offered as to the effect of heat is a change in the velocity of vibration, and it may well serve to explain the variations caused in valence.

Electricity.—Changes of valence due to electricity are probably not unusual but few observations concerning them have been recorded. One of the most noteworthy is the production of carbon monoxide from carbon dioxide by the passage of the electric spark.

$$CO_2 = CO + O.$$

Chemical Action.—The most usual method of bringing about a change of valence is by chemical action. When the change is from a higher proportion of the negative element to a lower it is commonly called *reduction*, and the reverse change is spoken of as *oxidation*. These terms are apparently relics of an older theory, and are confusing, especially to a student beginning the study of chemistry. They should be limited to cases of the actual removal or addition of oxygen. Thus, to speak of the change of ferrous to ferric chloride by the action of chlorine as an oxidation is careless and incorrect.

$$FeCl_2 + Cl = FeCl_3.$$

It is pushing the type theory rather far to speak of the salts of one valence as being derived from the oxide of that valence and yet this is frequently done.

When we take ferric chloride and let sulphurous acid act upon it, it is called a reduction of the ferric chloride to ferrous chloride, although certainly no oxygen is removed from the ferric chloride nor is oxygen added when the ferrous chloride is changed again to ferric chloride by the action of nitric acid, and still this is called an oxidation. The use of terms for these reactions is evidently in need of revision. What shall we call the following reaction, cited by Drechsel as an "oxidizing action?"

$$2KMnO_4 + 10FeSO_4 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O.$$

Some hydrogen is oxidized with the formation of water but that is not what is meant. The manganese is changed from its highest valency to its lowest and the iron from its lowest to a higher. The permanganate is of course deoxidized.

It seems that chemical action may induce change when to an existing molecule a third substance is offered capable of combining with one or more of its constituent atoms, thus releasing the former equilibrium. Thus when sulphurous acid takes the oxygen of water setting hydrogen free the hydrogen then takes one of the chlorine atoms held by the iron.

$$2FeCl_3 + H_2SO_3 + H_2O = H_2SO_4.2HCl + 2FeCl_2.$$

But the presence of all three of these molecules is needed for the reaction to take place. So too, potassium permanganate is stable in the presence of sulphuric acid, unless the ferrous sulphate or some such molecules are present. When molecules of these three substances come together there is immediate rearrangement of molecules with change of equilibrium. Whether we are dealing here with a play of affinity which causes the tumbling down of certain molecules and building up of others, or whether it is a question of vibratory equilibrium between these molecules, cannot yet be told. The only certain thing seems to be that a molecule containing bivalent iron and another containing septivalent manganese cannot exist in the presence of one another but must change, when possible, to trivalent iron and bivalent manganese.

As meagre as our present knowledge is, it does not seem to be a very hopeful task to enter the maze of changes of valence through chemical reactions with a view to clearing up the ideas as to the nature of valence.

Explanations Offered.—Victor Meyer and Riecke have supposed that a solution of the problem could be arrived at best by studying the phenomena of frictional electricity, contact electricity, pyro-electricity, and electrolytic conductivity. Most of those who have suggested hypotheses have based them upon a study of the carbon atom and its compounds and in particular its space relations. I have gathered together such of these hypotheses as have come to my notice and for fear of doing the authors an injustice shall present their views as far as possible in the original language.

The first in point of time is the hypothesis of van't Hoff.[1] I have not had access to the original but will give van't Hoff's views as presented by Rössing and by Ostwald. Rössing[2] quotes:

"Die einfachste Betrachtung lehrt, dass jede Abänderung von der Kugelgestalt zu grösseren Äusserungen der Anziehung nach bestimmten Richtungen führen muss, da sich das Atom an diesen Stellen so zu sagen besser annähern lässt. Jede derartige Form bedingt also eine gewisse Zahl Hauptanziehungsfähigkeiten, Valenzen.

"Wo nun obendrein noch die Art des gebundenen Atoms die Bindungskraft bedingt, wird auch die Zahl der hervortretenden Valenzen davon abhängig sein, somit beim Vergleich der Verbindungen eines bestimmten Elementes mit verschiedenen anderen öfters eine Änderung der Valenz auftreten.

"Wenn sich ein Atom um eine bestimmte Lage gleichmässig in allen Richtungen hin und her bewegt, ist eine Änderung der äusseren Form, somit auch von Affinität und Valenz, notwendige Folge.

"Zieht man jetzt in Betracht, dass die Schwingungsgrösse der Atombewegungen von der Temperatur bedingt wird, so führt obige Anschauung zu dem thatsächlich gestützten Schlusse dass Temperaturzunahme die Anzahl der Valenzen verkleinert, die Affinitätserscheinungen abschwächt, also die gegenseitige Atomwirkung allmählich zur einfachen Gravitationsäusserung zurückführt. Thatsache ist, dass es eine obere Temperaturgrenze gibt, wobei von chemischer Wirkung nicht mehr die Rede ist; Thatsache ist auch, dass im entgegengesetzten Falle die chemischen Erscheinungen sich ungeheuer komplizieren, zweifelsohne dadurch, dass bis dahin ubersehene Valenzen zur Geltung kommen.

"Die aufgestellten Betrachtungen ergeben als unmittelbare Folge, dass eine Atomvereinigung, ein Molekül, sich anderen gegenüber in der nämlichen Art und Weise, nur weniger scharf, äussert, wie das Atom selbst; auch das Molekül hat Affinität und Valenz, die zwar durch die eigenthümliche Zusammenstellung der Theile bedingt, nicht aber letzteren an und für sich eigen sind. So ergibt sich eine Grundlage für die Betrachtung der so-genannten Molekularverbindungen."

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[1] Ansichten über die organische Chemie, I, 3.

[2] Rössing: Theoretische Chemie, 180.

Ostwald[1] comments upon this hypothesis as follows :

"Es bleibt indessen noch eine Möglichkeit, die thatsächliche Verschiedenheit der Valenzwirkungen zu erklären. Wenn wir die Valenz als Frage einer Eigenschaft der Atome auffassen, deren Wirkung durch die Verschiedenheit der Zustande des Atoms insbesondere der Bewegungszustande, modifiziert werden kann, so ist es denkbar, dass obwohl die Ursache der Valenz unveränderlich ist, die Wirkungen dieser Ursache, eben die Valenz selbst, von Fall zu Fall verschieden erscheint.

"Eine Hypothese der erwähnten Art ist in der That von van't Hoff aufgestellt worden. Indem er annahm dass die chemische Anziehung zwischen den Atomen eine Folge der Gravitation sei, zeigte er, dass wenn ein Atom eine von der Kugelgestalt abweichende Form besitzt, die Intensität der Anziehung auf seiner Oberfläche eine bestimmte Anzahl Maxima besitzen müsse welche von der Form abhängt. Die Maxima können von verschiedenem Werte sein. Ist die Wärmebewegung des Atoms eine lebhafte, so werden nur die grösste Maxima ihre Atome festhalten können, und die Valenz zeigt sich, entsprechende der Erfahrung, bei höherer Temperatur kleiner als bei niederer."

Lossen's[2] idea as to valence, deduced from the consideration of the theories of van't Hoff and Wislicenus as to the space relations of the atom seem to be condensed into the single sentence:

"Diese Auffassung führt, nach meiner Meinung, nothwendig zu der Annahme, dass das mehrwerthige Atom sich überhaupt nicht als materieller Punkt betrachten lässt, dass vielmehr Theile desselben zu unterscheiden sind, von welchen die Wirkung auf andere Atome ausgeht."

Wislicenus[3] expresses his ideas as to valence as follows :

"Ich halte es nicht für unmöglich, dass das Kohlenstoffatom ein Gebilde sei, welches in seiner Gestalt einem regulären Tetraëder mehr oder weniger vielleicht recht sehr ähnelt : nicht für unmöglich ferner, dass die Ursachen jener Wirkungen, welche in den 'Affinitäts-einheiten' zur thatsächlichen Erscheinung kommen, sich in den Ecken dieses tetraëdrischen Gebildes concentriren, möglicherweise ähnlich und aus analogen Gründen, wie dies die elektrischen Wirkungen eines elektrisch geladenen

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[1] Lehrbuch der allg. Chemie, I ed. I, 830.

[2] *Ber. d. chem. Ges.*, 20, 3309.

[3] *Ibid.*, 21, 581.

Metalltetraëders thun würden. Die eigentlichen Träger dieser Energie würden schliesslich die Uratome sein, ganz wie die chemische Energie der zusammengesetzten Radicale unzweifelhaft eine Resultirende der den Elementaratomen innewohnenden Energie ist."

Victor-Meyer and Riecke[1] advance the following hypothesis:

"Auf Grund der mitgetheilten chemischen und physikalischen Erfahrungen haben wir uns nun folgende Vorstellung von der Constitution des Kohlenstoffatomes gebildet. Wir nehmen an, dass dasselbe umgeben ist von einer Aetherhülle, welche bei isolirten Atome, wie dieses selbst, kugelförmige Gestalt besitzt; das Atom selbst betrachten wir als den Träger der specifischen Affinitäten, die Oberfläche der Hülle als den Sitz der Valenzen. Jede Valenz denken wir uns bedingt durch das Vorhandensein zweier entgegengesetzter elektrischer Pole, welche in den Endpunkten einer im Vergleich zum Durchmesser der Aetherhülle kleinen geraden Linie befestigt sind. Wir bezeichnen ein solches System zweier elektrischer Pole als einen Doppelpol oder Dipol. Den vier Valenzen des Kohlenstoffatomes würden also vier solcher Dipole entsprechen. Die Mittelpunkte derselben denken wir uns gebunden an die Oberfläche der Aetherhülle, in dieser aber frei verschiebbar; die Dipole selbst seien freidrehbar um ihre Mittelpunkte."

It is scarcely necessary to give the further assumptions. The hypothesis of Knorr[2] may be also given in brief:

"Ich denke mir die Valenzen bedingt durch die Gliederung der Atome in besondere räumlich gesonderte Massen, die ich 'Valenzkörper' nennen will. Jeder Valenzkörper soll die Fähigkeit besitzen, andere Valenzkörper anzuziehen und durch diese Anziehung festzuhalten. . . . Die Werthigkeit ist bestimmt durch die relative Anzahl der in einem Atom vorhandenen Valenzkörper. Die Bindungen kommen zu Stande durch Berührung von Valenzkörpern. Im Kohlenstoffatom müssen die Valenzkörper gleichwerthig und gleichmässig im Raume gruppirt sein."

Flawitzky[3] takes as a basis for his hypothesis the suggestion of N. Beketoff that the cause of the chemical interaction of the

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[1] *Ber. d. chem. Ges.*, 21, 951.

[2] *Ann. Chem.* (Liebig), 279, 202.

[3] *Ztschr. anorg. Chem.*, 12, 182.

elements lay in the interference or coincidence of the motions of the atoms. The chief assumption is that the atoms of each element described closed curves which lie in planes, which are parallel to one another and have a constant absolute position in space. The atoms of different elements move in planes which make definite constant angles with one another. "Nehmen wir in der That an, dass die lebendige Kraft der Atome verschiedener Elemente gleich gross ist, so kann die Bewegung eines Atomes eines Elementes nur dann durch die Bewegung eines Atomes eines anderen Elementes vollständig aufgehoben werden, wenn die beiden Bahnebenen unter einander parallel sind. Widrigenfalls können je nach der Grösse des Winkels zwischen den Bahnebenen Fälle vorkommen, wo ein Atom eines Elementes dazu zwei, drei und mehr Atome eines anderen verlangen wird. Es können nämlich in solchen Fällen nur diejenigen Komponenten zur Wirkung kommen welche der Bewegungsebene des anderen Atoms parallel sind. Somit lässt sich die Wertigkeit der Elemente auf die Verschiedenheit der Winkel zwischen den Bahnebenen verscheidenartiger Atome zurückführen. Die Grössen dieser Winkel müssen augenscheinlich dem Gesetze ganzer rationaler Beziehungen folgen, wodurch die Fähigkeit der Atome, sich in ganzen Zahlen zu verbinden, bestimmt ist."

It is quite possible that other hypotheses as to valence have been formulated but have escaped my notice. These will suffice to give the more recent trend of thought upon the subject. I may state that none of these were known to me when the first paper was sent on for publication as I had not deemed it necessary to look beyond the usual text-books in examining into the literature upon the subject. This statement is not made for personal reasons as that is a matter of small moment, but that there may attach to my hypothesis whatever of value there is in the independent reaching of a conclusion.

It is not pertinent to this paper to discuss at any length the citations just given. But a few words are needed to bring out certain differences and distinctions. In most of them we have the assumption of some peculiar form of energy—an "Anziehungskraft." Flawitzky alone makes no explicit assumption of the kind. Besides this assumed force, which is the point of contention after all, we have various other assumptions of a remarkable character; *e. g.*, as to the forms of atoms, envelopes, primal atoms, and *Valenzkörper*. Flawitzky's hypothesis is based upon the angles made between the planes in which the atoms move.

Now in the place of all this I wish to substitute that which seems to me to be the simpler hypothesis of vibratory equilibrium.[1] There is only one attractive force to be considered and this is called chemical affinity and causes the union of the atoms, binding them together. These atoms may unite atom with atom, or one atom with two or three or more atoms of the other element or other elements. While we speak of union there is no actual contact to be assumed. The individual atoms have their own motion and at the same time the aggregation of atoms, or molecule, has a motion proper to it. The conditions of equilibrium in such a system determine the number of atoms which can enter it: as one to one, one to two, etc. There is no distinct force of valence determining this. The form of the atoms can scarcely be taken into consideration because the distance between the atoms is too great, compared with the mass of the atom, for the form to exert much influence, unless it influences the character of the motion. The atomic weight also has little influence in determining the number of atoms needed to satisfy the conditions of equilibrium except that there seems to be a general rule that with increase in the atomic weight in any one group more stable equilibrium is brought about with the smaller number of atoms and in a choice between several the lesser valence is preferred. (Compare nitrogen and bismuth; sulphur and tellurium.)

There would then appear to be seven, possibly eight, different kinds of motion among the atoms. Different velocities of vibration are not meant, but different phases of motion. For instance, all may have elliptical orbits with different focal distances; or circular, with different radii, etc. In any group of elements the motion of the atoms would have one common characteristic but there would be differences in velocity. In the first and seventh group, showing, for the most part, a tendency towards the same equilibrium, or having the same valence, the motion must be closely analogous. So too for the second and sixth groups, the third and fifth. There may then be a necessity for four distinct

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[1] Dr. Jas. Lewis Howe suggests the name "kinetic equilibrium."

phases only, unless we suppose a fifth for the eighth group. If the motion of an atom can be changed from one character to another its valence is changed and in such general properties as are dependent upon motion and not upon atomic weight it is equivalent to changing its group. Electricity, light, heat, and chemical action can cause this change of motion. In so far the properties of the element are subject to change and within our control. But the other factor, atomic weight, with the properties of the element determined by it, is not subject to change nor within our control, so far as our knowledge goes.

While it is freely granted that there is so much of the speculative in what has been said as to make us touch the whole subject with extreme caution, and while it is further admitted that it is quite beyond the reach of present experimental research, yet it is believed that the use of the imagination is legitimate and tends toward the advancement of the science so long as the true value is set upon it and fancy is not allowed to obscure fact nor to be mistaken for it. The hypothesis proposed is simple and if true will be very helpful. It will be a great step forward if it can be shown that the doctrine of valence is a doctrine of vibratory equilibrium.

EMETINE OCTOIODIDE AND THE EXTRACTION AND ESTIMATION OF ALKALOIDS GENERALLY.[1]

By H. M. Gordin and A. B. Prescott.

Received November 27, 1898.

In a previous paper[2] we have shown that most alkaloids form definite compounds when treated with excess of iodopotassium iodide and that it is possible to estimate the strength of aqueous solutions of alkaloidal salts by means of standardized solutions of iodine and of sodium thiosulphate. In applying this method to the assay of medicinal drugs it is immaterial what method of extraction of the alkaloids from the drug is employed, provided the final alkaloidal solution be sufficiently deprived of non-alkaloidal matter. The simplest and quickest method of obtaining the alkaloidal solution sufficiently free from foreign

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[1] In the work of Research Committee D, Section 2, Committee of Revision and Publication of the Pharmacopoeia of the United States. Read by title before the New York meeting of the American Chemical Society, December 28, 1898.

[2] This Journal. 20, 706, Sept., *1898*.

matter is undoubtedly the method proposed by Dr. A. B. Lyons.[1] This consists in macerating a weighed quantity of the powdered drug in a definite volume of Prollius' fluid with frequent shaking for several hours, drawing off an aliquot part of the clear liquid, evaporating and taking up the residue with acidulated water. The alkaloidal solution obtained by this method is generally almost perfectly colorless and can be worked up further for a gravimetric estimation by shaking out the alkaloids with chloroform and ammonia. For our iodometric method the filtered solution can be treated directly with excess of iodine, the excess of which is then estimated by sodium thiosulphate. For the alkalimetric estimation, again, the same filtered solution may be taken, using standardized acid in excess and estimating the excess by means of standardized alkali. The only drawback to this method of extraction is the great difficulty of preventing loss by evaporation of the highly volatile solvent, by which loss the volume of the aliquot part becomes reduced, and the final figure is liable to be too high.

A GENERAL METHOD OF EXTRACTION.

In order to avoid this difficulty we have worked out an entirely different method of alkaloidal extraction which can also be used with any one of the methods of estimation as desired. In its main features this method is the same as that which we proposed for the assay of opium.[2] It is carried out in the following manner :

One to four grams of the finely powdered drug is weighed into a low wide-mouthed vessel, with a round bottom, holding eight or ten ounces and having a well-fitted cork, such as a screw-top ointment-jar.[3] The powder is rubbed up with a small pestle to a fine paste by adding a little of a solvent mixture, composed of stronger ammonia water and alcohol each five cc., chloroform ten cc., and ether twenty cc. Then a few more cubic centimeters of this mixture are added, so as to have the drug well covered with the liquid, using in all about five times the amount of the drug taken. The vessel is corked, with the pestle inside, and is set aside for about four or five hours, taking care to agitate by

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[1] Manual of Pharm. Assaying, Haynes & Co., Detroit, Mich., *1886*, p. 20.

[2] This Journal, *1898*, 20, 724 ; *Pharm. Archives*, *1898*, p. 121.

[3] An ordinary teacup fitted with a specie cork answers well.

circular movement very frequently during that interval. After that time the cover is removed and the vessel kept in a current of air, stirring frequently till all odor of ammonia has disappeared. With a good draught and frequent stirring the powder will be almost perfectly dry in about two hours. The vessel is then put into a vacuum desiccator over sulphuric acid for about four or five hours.

An amount of powdered sodium chloride equal to about five or six times the amount of drug employed is then carefully mixed in, with use of the pestle, and the whole thrown into a small percolator, one provided with a glass stop-cock and having a plug of cotton at the bottom.[1] The vessel is then cleaned out several times with small quantities of sodium chloride, and the cleanings added to the percolator. The mixture in the percolator is then covered with a piece of cotton which is pressed down with a piece of glass, and a suitable menstruum, usually chloroform, is poured slowly into the percolator till the menstruum reaches the stop-cock. The latter is then closed, the percolator covered, and set aside for five or six hours. After that time the stop-cock is opened, and the drug exhausted with the menstruum percolating until ten drops of the percolate being evaporated on a watch-glass, and the residue taken up with a few drops of acidulated water, the solution shows no turbidity whatever on adding a few drops of Wagner's reagent. When finished the percolate, which is received in a flat evaporating dish, is placed in a good draught at a temperature of about 30° C. When the liquid is reduced to a very small volume, ten cc. of acidulated water[2] are added, and then a few cubic centimeters of ether, or petroleum ether, so as to have an ethereal liquid cover the aqueous solution,[3] when the whole is stirred with a glass rod until all the ethereal liquid is driven off. The liquid is then filtered and the evaporating dish and filter washed several times with acidulated water. In this way is obtained a colorless solution of the alkaloid, which can be worked up for any method of assay.

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[1] A suitable percolator is easily made out of an ordinary piece of glass tubing fitted with a perforated cork through which passes a tube having a glass stop-cock.

[2] If an alkalimetric assay is intended the acidulated water in the operation should be standardized and taken in definite quantities.

[3] If the menstruum is all evaporated off it is sometimes difficult to dissolve out the alkaloids with acidulated water. If chloroform be used, coming below the aqueous layer, it evaporates too slowly.

THE IODOMETRIC ESTIMATION.

In the periodide method of assay the final alkaloidal solution obtained, whether by our method, by Dr. Lyons' method, or by any other method, this final solution representing a definite quantity of the drug to be assayed, is poured slowly and with constant stirring into a flask holding 100 cc. in which has been previously drawn twenty or thirty cc. of a standardized solution of iodine and one or two cc. of dilute hydrochloric acid[1] (U. S. P.). The flask is then filled up to 100 cc., stoppered, and well shaken till the periodide has separated out. The supernatant liquid is to be perfectly transparent but of a red iodine color. Fifty cc. are then filtered off and in this portion the excess of iodine determined by means of standard sodium thiosulphate. The amount of iodine consumed multiplied by the suitable factor, gives the amount of alkaloid present in the quantity of drug taken.

In the case of several alkaloids being present in the drug a mean iodometric factor can be deduced in the same way as is done in the alkalimetric assay. It is to be noticed that should there be no precipitate with iodine, but only a slight turbidity, then the drug is extremely poor and for the assay a much larger quantity than one to four grams should be taken. On the other hand should the supernatant liquid, after adding the alkaloidal solution to the iodopotassium iodide solution and separating the periodide by shaking, have very little color or be almost colorless then it is certain that the drug is very rich, and either a smaller quantity of the drug or a larger quantity of the iodine solution must be employed in the assay.

The method of extraction described above presents particular advantages in those cases where several alkaloids soluble in different menstrua are present in the drug, as by using these menstrua successively, a separation of the alkaloids can be easily effected. This principle we have applied to the assay of opium, and it seems also to be applicable to *Hydrastis canadensis*, a report upon which we intend to publish in the near future.

This method of extraction of alkaloids for assay purposes has given us very good results with all drugs experimented upon,

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[1] Except in the case of morphine an excess of acid is not hurtful and even promotes the separation of the periodide. Hydrochloric is to be preferred to sulphuric acid.

except ipecac root. For some unaccountable reason it is almost impossible to extract free emetine, which is liberated in our process by the ethereoammoniacal mixture, from this root by percolation. Ether, chloroform, and acetone were tried as menstrua, but in all cases the result was much lower than that obtained by Lyons' process.[1] Though the percolation was not interrupted till a few drops tested in the general way with Wagner's reagent gave no reaction whatever. The very low result as compared with that obtained by Lyons' method shows conclusively that the exhaustion cannot be made complete by percolation. This fact would possibly explain why Flückiger[2], who extracted ipecac by percolation with ammoniated chloroform, obtained exceptionally low results.[3] In the assay of ipecac, given at the end of this paper, the method used was that of Dr. Lyons. The other drugs have been extracted by our method as described above, and the results compared with those obtained by Lyons' method.

The periodide assay method applied to nux vomica, along with a modification of Dunstan and Short's method of separation of strychnine from brucine[4] affords a convenient way of separate estimation of each of these alkaloids in the drug as follows:

The acidulated alkaloidal solution obtained from nux vomica in any suitable way, and representing four grams of the drug, is made up to a definite volume, say 100 cc. Of this solution twenty-five cc., which represent one gram of nux vomica, are run from a burette into a 100 cc. flask in which has been placed twenty cc. of decinormal iodine solution and two cc. dilute hydrochloric acid, and the amount of iodine consumed by the total alkaloids contained in that one gram nux vomica is reached in the way described above. Let that amount be *a*. If only the amount of total alkaloids in the nux vomica is desired it is sufficient to multiply *a* by 47.845 which is equal to 100 times the mean factor of strychnine and brucine and the percentage of total alkaloids is at once obtained.

THE SEPARATE ESTIMATION OF STRYCHNINE AND BRUCINE.

For the separate estimation of each of these alkaloids, another

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[1] It is Lyons' general method, not his modification of Dragendorff's method, that is referred to here.

[2] *Pharm. Ztg.*, *1886*, 30.

[3] See also Guareschi: Einfeuhr in d. Stud. d. Alkal., *1896*, 527.

[4] *Pharm. J. Trans.* (3), 14, 290; *Am. J. Pharm.*, *1883*, 579.

portion of the alkaloidal solution, representing two grams of the nux vomica, that is fifty cc., is run out from the burette into an Erlenmeyer flask of the capacity of about 300 cc. and to the contents of the flask ten cc. of a two per cent. solution of sulphuric acid is added, and then water enough to make in all about 200 cc. Then pour in twenty-five cc. of a five per cent. solution of potassium ferrocyanide, stopper the flask and shake continuously for about half an hour. Now filter, wash the precipitate on the filter repeatedly with water containing one per cent. of sulphuric acid, till a few drops of the filtrate diluted with a little water have no bitter taste. The filter is then pierced and the precipitate rinsed with use of the wash-bottle into a 100 cc. flask. To the contents of the flask are then added twenty cc. of a five per cent. solution of zinc sulphate, and the flask kept on a boiling water-bath for about fifteen minutes. The zinc sulphate decomposes the strychnine ferrocyanide, zinc ferrocyanide is precipitated, and strychnine sulphate remains in solution. The flask is then completely cooled, and water enough added to make 100 cc. Of this, fifty cc. representing again one gram of the nux vomica but deprived of the brucine, are then filtered off and run out from the burette into a 100 cc. flask containing twenty cc. decinormal iodine solution, and about two cc. of dilute hydrochloric acid. The amount of iodine consumed by the strychnine alone is then determined as above. Let it be b. Then $b \times 43.9$ (100 times the strychnine factor) gives the percentage of strychnine, and $(a - b) \times 51.79$ is the percentage of brucine in the nux vomica.

To test the exactness of this method we prepared a solution containing known quantities of each of these alkaloids and determined these by the described method. The results as can be seen from the following table are fairly satisfactory, if we consider the well-known difficulties of this separation.

The solution contained 0.16 per cent. strychnine and 0.22 per cent. brucine (anhydrous).

	Iodine consumed by 10 cc. before the removal of brucine.	Iodine consumed by 10 cc. after the removal of brucine.	Found.		Contained.	
			Strychnine.	Brucine.	Strychnine.	Brucine.
1 ……	0.0843132	0.032397	0.14	0.24	0.16	0.22
2 ……	0.0843130	0.032397	0.14	0.24	0.16	0.22

Following is a report of drugs which we have so far assayed both gravimetrically and iodometrically. The factors are those given for the higher periodides in our previous paper.[1] For nux vomica the mean factor was taken which is equal to 0.47845 parts of total alkaloids for one part iodine consumed. For ipecac root the factor 0.5453 is used which is based upon the fact that, as shown at the end of this paper, emetine forms a hydriodide heptiodide when treated with excess of iodopotassium iodide. Taking Lefort and Wurtz's formula for emetine we get

$$7 \times 126.53 : 482.98 :: 1 : \text{factor} = 0.5453.$$

The factors for the drugs of the table are as follows:

Mean factor of strychnine and brucine	0.47845
Atropine	0.2849
Emetine	0.5453

Drug.		Quantity taken for assay. Grams.	Iodine consumed.	Percentage of alkaloids. Iodometric.	Percentage of alkaloids. Gravimetric.
		NUX VOMICA.			
Iodometric	1	1	0.0526816	2.52	....
	2	1	0.0526725	2.52	....
Gravimetric	1	1	*	....	2.73
	2	1	*	....	2.73
		BELLADONNA ROOT.			
Iodometric	1	2.5	0.0459179	0.52	....
	2	2.5	0.0459263	0.52	....
Gravimetric	1	2.5	*	....	0.51
	2	2.5	*	....	0.51
		BELLADONNA LEAVES.			
Iodometric	1	5	0.0478286	0.27	....
	2	5	0.0475922	0.27	....
Gravimetric	1	5	*		0.28
	2	5	*		0.28
		IPECAC ROOT.			
Iodometric	1	2	0.0957764	2.61	....
	2	2	0.0986633	2.69	....
Gravimetric	1	2	*		2.63
	2	2	*		2.62

* Alkaloids shaken out and weighed.

Emetine Octoiodide.

Emetine seems to form with iodine two periodides, according to whether the iodine is added to the alkaloid or *vice versa*, but owing to the lack of material we have only isolated and analyzed

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[1] This Journal, (*1898*), 20, 724.

one; namely, the higher periodide. The emetine used was obtained from Merck & Co. The periodide was made by pouring 200 cc. of a solution of emetine in acidulated water, this solution containing about half a per cent. of the alkaloid, into about 500 cc. of a solution which contained about one per cent. of iodine with one and five-tenths per cent. of potassium iodide, and was strongly acidulated by hydrochloric acid. The mixture was shaken till the supernatant liquid became perfectly transparent, the precipitate was separated by means of the pump, quickly washed with cold water and then dried, first on porous plates and then *in vacuo* over sulphuric acid.

Thus obtained the periodide is a dark-brown powder, hardly soluble in benzene, ether, or chloroform, quite soluble in alcohol, and very soluble in a mixture of four parts of alcohol and one of chloroform. The chloroform greatly increases the solubility of the periodide in alcohol, though chloroform alone hardly dissolves it. So far we have not been able to recrystallize it. On evaporation of the solvent a viscous mass is generally left. Authorities differ with regard to the formula of emetine, as follows:

Lefort and Wurtz,[1]	$C_{28}H_{40}N_2O_5 = 482.98$
Glenard,[2]	$C_{30}H_{44}N_2O_4 = 494.96$
Kunz,[3]	$C_{30}H_{40}N_2O_5 = 506.92$
Paul and Cownly,[4]	$C_{15}H_{22}NO_2 = 247.48$

Our periodide corresponds best to the formula of Lefort and Wurtz. It seems to be an emetine hydriodide heptiodide, $C_{28}H_{40}N_2O_5.HI.I_7$.

For the estimation of the additive iodine the periodide is dissolved in chloroform mixed with alcohol and titrated with standardized sodium thiosulphate using starch as indicator. It is best to add first an excess of the thiosulphate solution, then add considerable water, when the excess is titrated back with standardized iodine. For the total iodine the periodide is dissolved in a little chloroform mixed with a few drops of alcohol; powdered zinc is then added and the mixture kept on a water-bath till effervescence (from the action of zinc on the chloroform)

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[1] *Ann. chim. phys.* (5), 12, 247.

[2] *Ibid.* (5), 8, 233.

[3] *Arch. d. Pharm.*, 225 (*1887*), 461; 232 (*1894*), 466.

[4] *Pharm. J.*, (3), 24, 61.

ceases. To the mixture, when cold, ammonia water is added, and the iodine in the zinc and ammonium iodide is estimated exactly as described in the analysis of morphine tetraiodide.[1]

For additive iodine 0.1492 gram of the periodide gave 0.0880045 gram iodine, and 0.122 gram gave 0.0727250 gram iodine.

	Calculated for $C_{38}H_{40}N_2O_6.HI.I_7$.	Found.
1	59.24	59.98
2	59.24	59.61

For total iodine 0.1313 gram of the periodide gave 0.0890502 gram iodine, and 0.12095 gram gave 0.0818797 gram iodine.

	Calculated for $C_{38}H_{40}N_2O_6.HI.I_7$.	Found.
1	67.69	67.82
2	67.69	67.69

CHEMICAL LABORATORY OF THE
UNIVERSITY OF MICHIGAN,
November 6, 1898.

NOTES ON THE RAPID DETERMINATION OF TUNGSTEN IN STEEL.[2]

BY GEORGE AUCHY.

Received November 3, 1898.

THE rapid method of determining tungsten in steel, generally in use and described in Blair's "Chemical Analysis of Iron," is as follows: Solution of the steel in aqua regia; evaporation to dryness; re-solution in strong hydrofluoric acid containing a little strong nitric acid; dilution and boiling; filtration and ignition of the tungstic oxide contaminated with silica and ferric oxide; elimination of the silica by hydrofluoric acid; ignition and weighing of the tungstic acid and ferric oxide; fusion with sodium carbonate; solution and filtration to determine the ferric oxide. If in this method the final steps—the fusion with sodium carbonate and the determination of the ferric oxide—could be dispensed with, evidently a very considerable saving of time and trouble in the performance of the method would be made; and it has doubtless been observed by many members of the society having occasion to make tungsten determinations in steel, that within the range of their experience the ferric oxide thus carried down with the tungstic acid is constant in amount or nearly so. If this uniformity exists in all steels containing every percentage of tungsten, of course, the determination of

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[1] This Journal, *1898*, 20, 717.

[2] Read by title before the New York meeting of the American Chemical Society, December 28, 1898.

this ferric oxide contamination in every particular instance is unnecessary. One of the objects of this paper is to suggest that if members of the society having to do with tungsten in steel, would gather from their note-books, and publish the data representing the amounts of ferric oxide found contaminating their tungstic acid precipitates, the uniformity of these ferric oxide contaminations would no doubt be shown and result in the improvement of the method. The writer's own experience is confined to steels containing 0.20 per cent. to 1.75 per cent. tungsten, and indicates that the ferric oxide contamination is always practically the same within those limits, and that the amount, with four grams steel[1] taken for analysis and with varying amounts of acid present in solution, is about 0.03 per cent. in terms of tungsten. Results follow :

Five cc. Free Hydrochloric Acid Present in Solution.

No.	Tungsten. Per cent.	Ferric oxide in terms of tungsten. Per cent.
70	1.110	0.036
504	0.230	0.022
137	1.710	0.032
585	0.250	0.022
352	0.428	0.016
586	0.255	0.022
353	0.434	0.022
587	0.350	0.022
49	1.230	0.032
588	0.375	0.026
51	1.240	0.034
589	0.260	0.028
52	1.240	0.028
590	0.335	0.027
154	1.160	0.028
591	0.310	0.022
346	0.482	0.024
352	0.442	0.020
353	0.434	0.020
363	0.466	0.020
364	0.444	0.020
154	1.090	0.036
380	0.428	0.028
411	0.430	0.026
412	0.400	0.022
179	1.250	0.028

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[1] 3.9655 grams. Weight of WO_3 multiplied by twenty gives percentage of tungsten in the steel.

TEN CC. FREE HYDROCHLORIC ACID PRESENT IN SOLUTION.

No.	Tungsten. Per cent.	Ferric oxide in terms of tungsten. Per cent.
179	1.25	0.028
49	1.25	0.028
51	1.25	0.030
52	1.27	0.030
70	1.00	0.028
137	1.65	0.032
154	1.10	0.034
179	1.22	0.042
70	1.08	0.022
352	0.384	0.020
353	0.396	0.020
70	1.100	0.026
179	1.230	0.026
352	0.396	0.028
353	0.390	0.030

More accurately speaking, the amount of ferric oxide contamination lies between 0.02 and 0.03 per cent. for the lower percentages of tungsten and between 0.03 and 0.04 per cent. in steels containing from 1.00 to 2.00 per cent. tungsten. In these tests the ferric oxide in the sodium carbonate used for fusion was found and deducted. Also regard was had for the fact that the weight of the crucible is sometimes slightly affected by the fusion.

Professor Arnold in his "Steel Works Analysis" directs that the tungstic acid be washed with very dilute hydrochloric acid till quite free from iron; and omits the sodium carbonate fusion for the determination of the iron. In the above tests the tungstic acid precipitates were washed seven times with hot hydrochloric acid (1 : 20) and three times with alcohol (1 : 4) filling the filter each time. In one case only 0.10 per cent. tungsten carried down 0.012 per cent. ferric oxide, in terms of tungsten, not washed out by this procedure.

The determination of silicon in tungsten steels is most conveniently made along with that of the tungsten.

PRECAUTIONS IN TUNGSTEN DETERMINATIONS.

Authorities do not agree in considering the completeness of the tungstic acid separation to be affected by the acidity of the liquid from which it separates. For instance, in Blair's

"Chemical Analysis of Iron," the dry residue after the dehydration of the silica is directed to be taken up with an amount of strong hydrochloric acid sufficient for the purpose (about forty cc. for four grams steel, and ten cc. for one gram), and then, without any previous evaporation or neutralization, diluted, boiled, and filtered. In Arnold's "Steel Works Analysis," on the contrary, the liquid is directed to be evaporated to a bulk of five cc. before dilution and filtration. Another point that does not seem to be generally appreciated is that evaporation to dryness and dehydration of silica from nitric acid solution does not always cause complete separation of the tungstic acid, although such an evaporation and dehydration from hydrochloric acid solution will separate all the tungstic acid. In Blair's description of the standard method the evaporation and dehydration is made in nitric acid solution.[1] In Arnold's method the evaporation and dehydration from nitric acid solution is also made, but is followed by a second evaporation to dryness from hydrochloric acid solution, the explanation being made that several evaporations to complete dryness are necessary to insure the complete separation of the tungstic acid on account of its solubility in hydrochloric acid.

With regard to these two points it is the writer's experience that the completeness of the tungstic acid separation is dependent upon the smallness of the amount of acid present in the liquid; and frequently also upon whether the previous evaporation and dehydration has been made from nitric or from hydrochloric acid solution. The amount of acid in the liquid from which the tungstic acid is filtered should be as little as possible; and the preceding evaporation to dryness and dehydration of silica should be made in hydrochloric and not in nitric acid solution, in which case only one such evaporation to complete dryness is necessary. The best procedure seems to be: Solution of the steel in dilute nitric acid (taking four grams of the steel); evaporation to first appearance of a scum on the surface of the liquid; addition of thirty to forty cc. strong hydrochloric acid; evaporation to dryness and heating on the hot plate; re-solution in forty cc. strong hydrochloric acid; evaporation to first appearance of scum; taking up with five cc. strong hydrochloric acid diluted to twenty cc. with water,

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[1] In his rapid method the evaporation and dehydration is made from *aqua regia* solution.

and heating; addition of twenty-five to thirty cc. of hot water; and filtration.

The failure of a complete separation of tungstic acid by evaporation to dryness from nitric acid solution is perhaps due to the absence of aqua regia—aqua regia perhaps being necessary to a complete oxidation to tungstic acid. Blair, in fact, in his rapid method, dissolves the steel in aqua regia, and also takes up the dry residue with aqua regia containing, however, an unusual proportion of hydrochloric acid. But this theory is rather discredited by the fact that in Arnold's process no aqua regia is formed, the heating for the dehydration of the silica being carried to the point of decomposition of nitrates, and yet all the tungsten is obtained.

The following results illustrate the necessity for the two precautions just considered.

No	5 cc. HCl present. Total bulk 50 cc. Tungsten. Per cent.	[illegible]0 cc. HCl present. Total bulk 100 cc. Boiled before filtration. Tungsten. Per cent.	40 cc. HCl present. Total bulk 100 cc. Boiled before filtration. Tungsten. Per cent.
70	1.11	1.10	1.05
137	1.71	1.67	1.59
352	0.442 0.428	0.396	0.290
353	0.434 0.434	0.390	0.320
49	1.24 1.23	1.24	....
51	1.24	1.25	....
52	1.25 1.24	1.27	....
154	1.16	1.09	....
179	1.26 1.25	1.23	....

In the above tests the filtrates from the tungstic acid of the first column of results were tested for tungstic acid by evaporation to complete dryness with aqua regia. None was found in any test. In the above tests, the evaporations to dryness and the dehydrations of the silica were all made from hydrochloric acid solutions; but in the following determinations they were made from nitric acid solutions.

No.	Tungsten present. Per cent.	Tungsten found. Per cent.
70	1.11	1.08
179	1.26	1.15
352	0.440	0.384
353	0.434	0.396
70	1.11	1.00
137	1.71	1.65
154	1.16	1.10
179	1.26	1.22

But ten cc. hydrochloric acid instead of five cc. were present in the solution; and the lowness of the results may have been partly due to that fact. Comparing results obtained under like conditions as regards the amount of acid present we have:

No.	10 cc. HCl present. Evaporation and dehydration from HCl solution. Tungsten. Per cent.	10 cc. HCl present. Evaporation and dehydration from HNO_3 solution. Tungsten. Per cent.
70	1.10	1.08
179	1.23	1.15
137	1.68	1.65
352	0.396	0.384
353	0.390	0.396
70	1.10	1.00
154	1.09	1.10
179	1.23	1.22

In No. 79 the filtrate from the tungstic acid (1.15 per cent. tungsten) was found to contain 0.10 per cent. tungsten.

Phosphorus in Tungsten Steels.

In Arnold's "Steel Works Analysis" the operator is directed to separate and filter tungstic acid before determining phosphorus. In Blair's "Chemical Analysis of Iron" this is not specified and it is therefore, perhaps, to be inferred that phosphorus is to be determined as usual. The following tests were made, using the volumetric method:

No.	P after separating and filtering tungstic acid. Per cent.	P as usual; yellow precipitate stood less than 2½ hours. Per cent.	P as usual; yellow precipitate stood over night. Per cent.	P carried down by the tungstic acid in the first column of results. Per cent.
154	0.016	0.017	....	0.0007
179	0.025	0.026	0.029	0.0007
70	0.017	0.018	0.024	0.0007
137	0.020	0.023	....	0.0009
70	0.017	0.018	....	....
70	0.017	0.016	....	....
70	0.017	0.018	....	....
154	0.016	0.018	....	....
179	0.025	0.025	0.032	....
179	0.022	0.024	....	....

This indicates that in very low phosphorus steels at least, the determination may be made as usual, provided the yellow precipitate is not allowed to stand more than two and one-half hours. Also in neutralizing with ammonia, no excess must be used or tungstic acid will precipitate with the ferric oxide and remain undissolved by the nitric acid added to clear the solution. But the tendency seems to be toward higher results.

Ferrotungsten

is usually analyzed by roasting, followed by solution, filtration, fusion, and evaporation with acid. The writer, with a sample containing 35.25 per cent. tungsten, obtained low results by this method (twenty-nine and thirty per cent.), doubtless because only a single fusion was made, but had no difficulty when using the same method as for tungsten steels, except that aqua regia was used for a solvent.[1] The ferrotungsten apparently could not be completely decomposed by this means. A bright metallic residue was left, consisting, however, of almost pure tungsten, and readily oxidizing to tungstic oxide by ignition after filtration. In this procedure the preparatory roasting of the ferrotungsten is, of course, unnecessary. The ferric oxide and other contamination seems to be variable ; in nine determinations of five different ferrotungstens, it ranged from 0.28 per cent. to 1.60 per cent.

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF PURDUE UNIVERSITY.]

THE ABSORPTION OF METHANE AND ETHANE BY FUMING SULPHURIC ACID.[2]

BY R. A. WORSTALL.

Received October 17, 1898.

APPARENTLY one of the most firmly established facts has been that marsh-gas and its homologues are not acted upon either by fuming nitric or by fuming sulphuric acids. The indifference of methane and ethane to all reagents, especially to

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[1] The metal being treated first with strong nitric acid and heated, and the strong hydrochloric acid then added by degrees.

[2] Read by title before the New York meeting of the American Chemical Society, December 28, 1898.

fuming sulphuric acid, has been generally accepted as a fact and made a basis for the separation of the saturated from the unsaturated hydrocarbons in gas mixtures. Hempel, in his well-known book on gas analysis, states that no absorbent for methane is known; and a statement credited to Kolbe, and widely quoted, is to the effect that a mixture of fumic nitric and fuming sulphuric acids is without action on methane even at 150° C.

Apparently there has been but one observed instance of the absorption of a gaseous paraffin by fuming sulphuric acid. Orndorff and Young[1] found that propane made from isopropyl iodide by the copper-zinc couple was slowly soluble in cold fuming sulphuric acid, the absorption amounting to over fifty per cent. in fifteen days, the acid taking a deep red color. In a former communication[2] I have shown that the higher members of the marsh-gas series are acted upon by fuming sulphuric acid, the products being true sulphonic acids. The peculiar fact brought out during this work that each hydrocarbon sulphonated at its boiling-point, suggested the idea that the gaseous members of the series would be soluble in cold fuming sulphuric acid, and this has been found to be the case.

METHANE.

1. *From Methyl Iodide.*—The methane employed in the first series of experiments was made from pure methyl iodide by the copper-zinc couple of Gladstone and Tribe.[3] The gas produced by the reaction was washed by passing through fuming sulphuric acid and was then allowed to stand over fuming sulphuric acid for three hours to free it of alcohol vapors. A portion was then measured off with the measuring burette and the absorption determined by passing it into the usual glass bead absorption pipette, filled with fresh fuming sulphuric acid.

In using this apparatus it is easy to so manipulate that after the gas has all been transferred to the absorption pipette, the bend in the capillary tube of the latter shall be filled with the acid, thus forming an effectual seal which prevents the gas from coming in contact with rubber connections. These rubber con-

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[1] *Am. Chem. J.*, 15, 261

[2] *Am. Chem. J.*, 20, 664.

[3] *J. Chem. Soc.*, *1884*, 154.

nections were renewed frequently and the apparatus frequently tested for leaks with measured quantities of air. Two different absorption pipettes were used and any errors from leakage are highly improbable. The gas was each time run into a caustic potash pipette before a reading was made, in order to remove all acid vapors.

The data obtained in the first series are as follows :

Time between readings.	Observed volume. cc.	Loss. cc.	Loss. Per cent.
0	84.5	....	....
30 min	84.4	0.1	0.12
4 hours	79.0	5.4	6.39
2 "	77.3	1.7	2.01
12 "	74.0	3.3	3.90
24 "	67.2	6.8	8.04
5 days	56.2	11.0	13.01
1 day	54.0	2.2	2.60
2 days	49.9	4.1	4.85
1 day	46.1	3.8	4.48
11 days		38.4	45.40

The residue of 46.1 cc. was sealed into the pipette and allowed to stand over the fuming sulphuric acid during the three summer months. At the end of that time it had lost 22.2 cc., the residue amounting to only 23.9 cc. of the original 84.5 cc.—a total loss of 71.7 per cent. The color of the acid had changed from a light straw to a cherry-red and the absorption was still going on.

A comparison of the absorption figures in the above and in the following table shows apparent irregularities and discrepancies in the absorption at different periods for the same interval of time. This is easily accounted for by the variation in the barometer and thermometer on these different days, and for which variations no corrections were made when volumes were read, while the fact that the methane from methyl iodide shows a larger average daily absorption than that from natural gas is doubtless largely due to the much hotter weather prevailing during the former tests.

2. *From Natural Gas.*—The experiments with methane were repeated, using natural gas as the source of methane. The natural gas is piped to Lafayette from eastern Indiana, and analyzed as follows :

	Per cent.
Hydrogen sulphide and carbon dioxide	1.80
Oxygen	0.70
Heavy hydrocarbons	0.50
Carbon monoxide	0.60
Hydrogen	0.55
Nitrogen	3.80
Methane	92.05
	100.00

In a recent article by Prof. Phillips,[1] attention was called to the occurrence of hydrogen sulphide in a Canadian natural gas. This Indiana natural gas also contains large quantities of hydrogen sulphide, sufficient to give a pronounced odor to the gas and to rapidly precipitate a solution of lead acetate.

About 110 cc. of this natural gas were measured off and all constituents save nitrogen and methane removed by the ordinary method of gas analysis, using palladium sponge to remove hydrogen. The residue therefore consisted of ninety-six per cent. methane and four per cent. nitrogen.

The absorption was carried out as before described with the following results :

Time between readings.	Observed volume. cc.	Loss. Per cent.
0	100.00	....
16 hours	98.5	1.5
7 "	98.0	0.5
1 day	95.5	2.5
"	94.0	1.5
"	92.6	1.4
"	90.9	1.7
"	90.1	0.8
"	89.5	0.6
"	88.4	1.1
"	88.1	0.3
"	86.7	1.4
"	85.4	1.3
"	83.6	1.8
"	82.5	1.5
"	82.2	0.3
"	80.8	1.4
"	77.5	3.3
"	75.7	1.8
17 days		24.3

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[1] This Journal, 29, 696.

That is, after remaining in contact with the fuming acid for seventeen days, a loss of 24.3 per cent. resulted,—an average daily absorption of one and four-tenths per cent. The residue was then sealed into the absorption pipette and allowed to stand three months during the winter. At the end of that time the total absorption amounted to 30.9 per cent.

ETHANE.

The ethane employed was made from pure ethyl iodide by the copper-zinc couple, washed by passing through fuming sulphuric acid, and was then allowed to stand for eighteen hours over fuming sulphuric acid to free it of all alcohol vapors. The absorption was carried out in the manner described for methane with the following results:

Time between readings.	Observed volume. cc.	Loss. cc.	Loss. Per cent.
0	95.0	....	....
1 day	91.3	3.7	3.89
"	84.7	6.6	6.95
"	79.5	5.2	5.47
"	75.8	3.7	3.89
"	70.2	5.6	5.89
"	65.0	5.2	5.47
"	61.1	3.9	4.10
"	57.3	3.8	4.00
"	53.2	4.1	4.32
"	48.2	5.0	5.26
"	43.0	5.2	5.47
"	39.5	3.5	3.68
"	36.2	3.3	3.47
"	32.0	4.2	4.42
"	28.0	4.0	4.21
15 days		67.0	70.5

In fifteen days, therefore, the absorption of ethane amounted to 70.5 per cent.,—an average daily absorption of 4.7 per cent. The residue was sealed into the pipette and allowed to remain in contact with the fuming acid for three months. At the end of that time the total absorption amounted to 88.3 per cent. As may be seen by comparison, the absorption of ethane is much more rapid than that of methane. Some oxidation results during this absorption, as carbon dioxide and sulphur dioxide are always produced. From the change in color of the acid it is probable that a sulphonic acid is also formed.

These results, establishing as they do the fact that methane and ethane are soluble in fuming sulphuric acid, are not without importance in their bearing toward gas analysis. A number of experiments were tried to determine the amount of absorption of each gas that took place in short intervals of time. After twenty-five per cent. of the methane obtained from natural gas had been absorbed, the residue was tested by measuring its absorption each hour. The results showed this absorption to be very slight, less than one-tenth cc. per hour. In the case of ethane, however, after over sixty per cent. had been absorbed, a similar series of experiments gave an average hourly absorption of 0.25 cc. equivalent to 0.60 per cent. of the ethane present.

In ordinary technical gas analysis, therefore, when the gas contains methane but no ethane, the absorption in the fuming sulphuric acid could be allowed to continue for an hour if necessary without much danger of serious error. But if ethane is present, fifteen minutes is the probable maximum of safety, and in any case the safest course to follow, especially in the case of an unknown gas, would be to shorten the time of contact with fuming sulphuric acid to the lowest possible limit.

LAFAYETTE, IND., October, 1898.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORIES OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY.]

THE VELOCITY OF THE REACTION BETWEEN SILVER ACETATE AND SODIUM FORMATE. A REACTION OF THE THIRD ORDER.[1]

BY ARTHUR A. NOYES AND GEORGE T. COTTLE.

Received October 28, 1898.

I. OBJECT OF THE INVESTIGATION.

THE investigations hitherto made of the velocities of those reactions in which two or more molecules of a substance enter have not yielded results of a general character. In many cases the velocity has been found proportional simply to the concentration of the substance, while in others it has been found proportional to that power of its concentration which corresponds to the number of its molecules entering into the reaction, as theoretical considerations would appear to demand. Thus, for ex-

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[1] Read before the Boston meeting of the American Chemical Society, August 25, 1898.

ample, the reactions between iron salts and potassium chlorate,[1] between hydrogen peroxide and potassium iodide[2], and between potassium bromate and potassium iodide[3], in the presence of an excess of acid, are all simple reactions of the second order, although three or more molecules take part in the chemical change. In two cases, on the other hand, have the number of reacting molecules shown their influence; namely, that of the polymerization of cyanic acid,[3] and that of the reaction between stannous chloride and ferric chloride,[4] both of which, in correspondence with the number of reacting molecules, follow the law of the third order.

Further investigations of such reactions are therefore necessary. A new, and, it would seem, a suitable, example is the reaction between silver acetate and sodium formate, and we have, therefore, measured its velocity. The reaction is expressed by the following equation:

$$2AgC_2H_3O_2 + HCO_2Na = 2Ag + CO_2 + HC_2H_3O_2 + NaC_2H_3O_2$$

or, more correctly, according to the dissociation theory:

$$2\overset{+}{Ag} + H\overset{-}{C}O_2 = 2Ag + CO_2 + \overset{-}{H}.$$

Thus it is a simple trimolecular reaction and should apparently follow the law of the third order, if any such reaction does so. We have selected a salt of formic acid in place of the acid itself and a silver salt of a very weak acid, in order to eliminate as far as possible the catalytic effect of the hydrogen ions.

II. DESCRIPTION OF THE EXPERIMENTS.

The sodium formate and the silver acetate used were prepared by recrystallizing the commercial salts, their purity being assured by qualitative tests. An exactly normal solution of the first, and a nineteenth normal of the second were made. The strength of the former solution was determined by addition of hydrochloric acid to a known amount in a platinum dish, evaporating to dryness, and weighing the residue; that of the latter by titration with potassium thiocyanate.

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[1] Hood: *Phil. Mag.*, (5), 6, 371; 8, 121; 20, 323; Noyes and Wason: *Ztschr. phys. Chem.*, 22, 210.

[2] Noyes and Scott: *Ztschr. phys. Chem.*, 18, 118.

[3] Van't Hoff: Etudes de Dynamique Chimique, S. 90.

[4] Noyes: *Ztschr. phys. Chem.*, 16, 546.

As the velocity of the reaction is very small at ordinary temperatures, we carried on the experiments at 100°. For this purpose we constructed a steam thermostat out of a cylindrical tin can. In the cover, before it was soldered on, were cut one small hole, for a ball condenser, and five large holes, two inches in diameter, provided with quarter-inch tin collars covered with rubber tubing. In these were then placed large 225 cc. test-tubes containing the measured amounts of silver acetate solution and of water. In the cases where the concentration of the silver solution was 0.100 normal, solid silver acetate was weighed directly into the tube and the necessary amount of water added, as so strong a solution of the salt cannot be prepared in the cold. Each of the large tubes was then fitted with a cork through which were passed a small twenty-five cc. test-tube containing the required amount of formate solution and of water, a thermometer, an efficient glass stirrer, and tubes for blowing out samples. The water in the bottom of the thermostat was kept boiling constantly, and when the temperature of the solution had become quite constant, the bottom of the small tube was broken by a glass rod, the two solutions immediately mixed by violent stirring, and the time (to the second) noted. At definite moments samples of the mixture were blown out into measured amounts of ice-cold standardized potassium thiocyanate solution, thus instantly stopping the reaction. As the flasks containing the thiocyanate were weighed before and after addition of the sample, the amount of the latter was easily determined. The end-point was then determined after filtration by titration with silver nitrate and potassium thiocyanate solutions, using ferric alum as an indicator. Thus the silver content of the mixture and the progress of the reaction were ascertained.

III. EXPERIMENTAL RESULTS AND VELOCITY CONSTANTS.

The results of the experiments and the calculated velocity-constants are found in the following tables. All experiments were carried out at the temperature of water boiling under atmospheric pressure. A expresses the original concentration of the sodium formate, and B that of the acetate. Under t are found the time in minutes reckoned from the moment of mixing. Under $(B-x)_1$ and $(B-x)_2$ are given the concentrations of the silver acetate found in two separate experiments after the time t, and under $B-x$ will be found the average of these results. Under C_2 and C_3 are given the constants of the second and of the third order respectively which occur in the equations:

$$\frac{dx}{dt}=C_2(A-x)(B-x) \text{ and}$$

$$\frac{dx}{dt}=C_3(A-x)(B-x)^2.$$

They are calculated, of course, from the corresponding integrated equations.[1] At the foot of each column of the C_2 values, is given the value, obtained by interpolation, corresponding to the time when the reaction is one-half completed. Under each column of C_3 values, the mean of the same is given.

FIRST SERIES.

$A=0.100$; $B=0.100$.

t.	$(B-x)_1$.	$(B-x)_2$.	$B-x$.	C_2.	C_3.
2	0.06694	......	0.06694	2.57	30.8
4	0.05334	......	0.05334	2.19	31.3
6	0.04684	......	0.04684	1.89	29.6
9	0.03784	......	0.03784	1.83	33.3
14	0.03235	......	0.03235	1.61	30.6
				2.05	31.1

SECOND SERIES.

$A=0.100$; $B=0.050$.

2	0.03774	0.03776	0.03775	1.51	34.9
4	0.03090	0.03080	0.03085	1.35	35.1
7	0.02455	0.02425	0.02440	1.20	35.9
11	0.01959	0.01958	0.01959	1.04	35.6
17	0.01519	0.01483	0.01501	0.91	36.7
				1.22	35.6

THIRD SERIES.

$A=0.050$; $B=0.100$.

2	0.08112	0.08093	0.08103	2.67	29.9
4	0.07180	......	0.07180	2.49	30.2
7	0.06395	......	0.06395	2.36	31.2
11	0.05920	......	0.05920	2.11	29.7
16	0.05625	......	0.05625	1.88	28.0
				2.56	29.8

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[1] Cf. Fuhrmann: *Ztschr. phys. Chem.*, 4, 89.

FOURTH SERIES.

$A = 0.050;\ B = 0.050.$

t.	$(B-x)_1$.	$(B-x)_2$.	$B-x$.	C_2.	C_3.
3	0.04019	0.04047	0.04033	1.60	35.8
8	0.03145	0.03173	0.03159	1.46	37.6
16	0.02473	0.02463	0.02468	1.28	38.8
25	0.02033	0.02066	0.02048	1.16	37.6
45	0.01629	......	0.01629	0.92	37.4
80	0.01250	......	0.01250	0.75	37.5
				1.29	37.4

FIFTH SERIES.

$A = 0.050;\ B = 0.0250.$

3	0.02192	......	0.02192	0.91	38.7
5	......	0.02004	0.02004	0.94	40.2
11	0.01634	......	0.01634	0.85	43.0
12	......	0.01579	0.01579	0.85	43.6
23	0.01194	0.01190	0.01192	0.76	45.8
				0.77	42.3

SIXTH SERIES.

$A = 0.0250;\ B = 0.050.$

10	0.03766	......	0.03766	1.49	37.3
25	0.03136	......	0.03136	1.44	38.6
45	0.02840	......	0.02840	1.27	37.3
80	0.02653	......	0.02653	1.08	34.4
				1.49	36.4

SEVENTH SERIES.

$A = 0.0250;\ B = 0.0250.$

10	0.02024	0.02009	0.02017	0.96	42.9
25	0.01626	0.01623	0.01624	0.86	43.8
45	0.01297	0.01276	0.01286	0.84	49.3
80	0.01140	0.01120	0.01130	0.61	39.0
				0.67	43.7

IV. DISCUSSION OF THE RESULTS.

Let us now consider the significance of the experimental results. In order to ascertain the order of a reaction and the influence of the individual substances upon its velocity, there are, as is well known, two different methods.[1] The first of these methods consists in determining the degree of the differential equation whose constants show the least variation during a sin-

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[1] Cf. Noyes : *Ztschr. phys. Chem.*, 18, 119 ; 22, 215.

gle experimental series. A brief glance at the preceding tables suffices to show that, in every series, the values of C_2 exhibit a constant, and as a rule very considerable, diminution during the progress of the reaction. On the other hand, the tables also show that the values of C_3 remain practically constant. The reaction, judged by this method, is therefore one of the third order.

The second method of determining the order of a reaction consists in degree of the equation whose constants retain nearly the same value in *independent* series of experiments with very different original concentrations. This method is much more reliable than the former, because the effect of disturbances, such for example as the influence of the products of the reaction upon the velocity, in comparison with the much greater effect of the large variations in the original concentration, becomes of no consequence. In order to show more distinctly the results obtained by the application of this second method to the reaction considered here, we present the following table, in which the comparable values of the constants of both orders derived from the seven experimental series are given. Under C_3 the mean values are shown, while under C_2 the values are given which correspond to the state of the reaction in which one-half of the substance present in smallest amount has undergone change.

Series. No.	Normal concentration of Sodium formate.	Silver nitrate.	C_2.	C_3.
1	0.100	0.100	2.05	31.1
2	0.100	0.050	1.22	35.6
3	0.050	0.100	2.56	29.8
4	0.050	0.050	1.29	37.4
5	0.050	0.025	0 77	42.3
6	0.025	0.050	1.49	36.9
7	0.025	0.025	0.67	43.7

It is evident that the values of C_3 in all seven of the series are approximately the same, while those of C_2 vary about 280 per cent., which proves that the reaction is essentially one of the third order, and that its velocity is nearly proportional to the concentration of the sodium formate and to the square of the concentration of the silver acetate. In the case of this reaction, therefore, the two methods for the determination of the order of a reaction, lead to the same conclusion.

Still, we must not leave unmentioned the fact that the proportionality between the velocity and the square of the concentration of the silver acetate is not absolutely exact. While the change of the original concentration of the formate exerts no definite influence upon the constants of the third order, yet, as will be seen from the last table, there occurs with every diminution of the original concentration of the silver salt, a slight, but still unmistakable, increase in the values of the constants C_3. As to the cause of this phenomenon, nothing can be said with certainty. It is not improbable, however, that the greater velocity in the more dilute solutions depends upon the greater dissociation of the silver salt, it being then assumed that only the silver ions are capable of reacting.

V. SUMMARY.

By this research it is established that the reaction between sodium formate and silver acetate proceeds with a velocity which is proportional to the concentration of the former salt, and nearly proportional to the square of the concentration of the latter. As this reaction, according to prevailing molecular ideas, takes place between one molecule of the formate (or of its anion) and two molecules of silver acetate (or of its silver ion), its observed velocity is in accordance with the theoretical requirements, and it furnishes a new confirmation of the influence of the number of the molecules taking part in reactions.

COUMARIN AND VANILLIN, THEIR SEPARATION, ESTIMATION AND IDENTIFICATION IN COMMERCIAL FLAVORING EXTRACTS.[1]

BY WILLIAM H. HESS AND ALBERT B. PRESCOTT.

Received November 27, 1898.

IT is a common practice in preparing an extract of vanilla from vanilla beans, to introduce also, as a lower-priced material, a portion of tonka beans. This makes a cheaper article and one that is generally popular with consumers. It is understood, however, to be an inferior article when compared with the genuine, and it can no longer be correctly labeled "Vanilla Extract." Under this name the presence of tonka extract constitutes an adulteration and hence the separation, identification, and esti-

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[1] Read by title before the New York meeting of the American Chemical Society, December 28, 1898.

mation of coumarin, the odoriferous principle of the tonka bean, has become a practical problem for the analytical chemist.

THEORY FOR THE SEPARATION OF COUMARIN FROM VANILLIN.

Vanillin is hydroxymethoxybenzoic aldehyde, while coumarin is the anhydride of coumaric (orthohydroxycinnamic) acid. The separation depends on the aldehydic character of vanillin. If vanillin be dissolved in pure dry ether and dry ammonia gas passed through the solution, the aldehyde ammonia compound of vanillin will be precipitated in almost quantitative proportions. It is accordingly not very soluble in ether; but like all aldehyde ammonias it is very soluble in water. Ammonia water should, then, extract all the vanillin from an ether solution. This theoretic principle is fully borne out in practice, as has been proved by repeated experiment. Coumarin, on the other hand, remains wholly in the ether solution.

METHOD OF ANALYSIS.

A sample of 25 to 100 grams of the commercial extract to be examined is placed in an evaporating dish, and the alcohol is allowed to evaporate at about 80° C. Water is added from time to time to keep the amount of liquid about equal to the original volume. When the alcohol is all gone, normal lead acetate solution is added drop by drop until no more precipitate forms. Stirring with a glass rod aids in the flocculation and settling of the precipitate. The solution is now filtered, best through an asbestos funnel under pressure, and the precipitate washed with a few cubic centimeters of hot water. The cooled filtrate is now extracted with ether[1] by shaking out in a separatory funnel. About fifteen to twenty cc. of ether are used each time, and the process of shaking out is repeated until a few drops of the ether evaporated on a watch glass leaves no residue. If the shaking is done thoroughly, three to four times' shaking out will usually be sufficient to extract all the vanillin and coumarin. The combined ether extracts are introduced into a second separatory funnel and shaken out with dilute ammonia (one part strong ammonia to two parts of distilled water) using about two cc. of the alkaline water solution at a time, and repeating the

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[1] Chloroform may be used instead of ether here and throughout the process, with this advantage that the evaporation of the chloroform leaves the residue dryer than it is when ether is used.

process until the ammoniacal solution is no longer colored yellow. The ether solution is washed with two cc. of water and this wash-water added to the alkaline extract. The ammoniacal solution is set aside for the estimation of vanillin. The ether solution is now poured out into an evaporating dish, and the ether allowed to evaporate spontaneously, or better, the dish containing the ether is placed in a vacuum desiccator over sulphuric acid, when the ether may be removed quickly. To prevent bumping of the ether and consequent loss during distillation *in vacuo*, a capillary tube sealed at one end is so placed in the liquid that the open end projects into the centre of the solution, while the sealed end extends well out of the liquid, and rests on the side of the dish. It is necessary that the tube be long enough to prevent its resting horizontally on the bottom of the dish.[1]

For Coumarin.—The residue having been left *in vacuo* over sulphuric acid long enough to remove all water, or else dried in an air-bath at not above 45° C., is treated with a few cubic centimeters of cold ligroin,[2] the latter being poured off into a clean dry weighed dish. The extraction with ligroin is repeated until a drop evaporated on a watch-glass leaves no residue. The ligroin is allowed to evaporate (best *in vacuo* in a desiccator containing paraffin), is dried at not above 45° C. and weighed. This gives pure crystalline coumarin, melting at 67° C. After weighing, a melting-point determination should be taken, and this, with the odor which is characteristic at this point in the analysis when compared with that of a known sample, is sufficient for its identification.

For Vanillin.—The ammoniacal solution obtained above is rendered slightly acid with ten per cent. hydrochloric acid. It is then shaken out with ether in the manner stated before. The ether is removed and the residue is dried *in vacuo* over sulphuric acid or else in an air-bath at not above 55° C. This residue is washed repeatedly with boiling ligroin, using a few cubic centimeters at a time to remove the vanillin and free it from adhering substances. The ligroin solution is decanted into a weighed

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[1] Tiny capillary tubes are very useful in preventing bumping in boiling liquids, and are made by drawing out a glass tube to the dimensions of a hair. Cut the tube into a convenient length and fuse up one end.

[2] A petroleum fraction boiling between 30° and 40° C.

dish, the ligroin is removed, the vanillin is dried at not above 55° C. and weighed. This gives a pure crystalline product, melting at 80°–81° C. After the weighing, a melting-point determination should be made, and then color tests may be applied. Some samples of vanilla extracts have been found to contain phenol-like bodies resembling creosol in odor and chemical behavior. These give color compounds with salts of iron; hence, any volumetric estimation, or even qualitative test, applied to the unpurified extract may be fallacious when based on color reactions of iron salts.

Results were obtained by this method under control as follows: From Mexican vanilla beans, a liquid product was made by following the directions of the United States Pharmacopoeia. Of this tincture, twenty-five grams were taken in duplicate portions; to each was added five-tenths gram of pure crystallized coumarin, and the analysis was made for estimation of coumarin and of vanillin. The coumarin recovered from the duplicate portions was, respectively, 0.491 gram or 98.2 per cent. of that taken, and 0.482 gram or 96.4 per cent. of that taken. The vanillin recovered was, respectively 3081 gram and 2997 gram, from each of the portions of twenty-five grams of the tincture.

This method for vanillin is much easier and quicker to work than the sodium bisulphite method, and has these advantages: (1) the shaking out with ammonia water is quickly done; (2) the alkaline solution of vanillin thus obtained is small in bulk; (3) the trouble of getting rid of sulphur dioxide is avoided. The separation of the vanillin is also more complete.

UNIVERSITY OF MICHIGAN,
November 18, 1898.

NEW METHOD FOR THE PREPARATION OF CESIUM.[1]

BY HUGO ERDMANN AND A. E. MENKE.

Received October 19, 1898.

WINKLER[2] tried to reduce cesium carbonate with metallic magnesium, in both glass and porcelain tubes in a current of hydrogen. He, however, obtained no cesium. Beketoff[3] states that it can be obtained in small quantities by the electrolytic reduction of the cyanide; he also acted on the hydrate with aluminum, but the yield was poor. In 1894 he

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[1] Read by title before the New York meeting of the American Chemical Society, December 28, 1898.

[2] *Ber. d. chem. Ges.*, 23, 53.

[3] *Bull. Acad. Petersburg*, 4, 247.

made a small amount by acting on cesium alum with metallic magnesium.[1] We made a great many experiments with a view to improving these processes, but finally found that a different method worked remarkably well, and if the directions are exactly followed it is absolutely free from danger. We found that by heating cesium hydroxide with magnesium powder in a red-hot tube through which passed a current of hydrogen, we could obtain nearly the theoretical amount of cesium. Inasmuch as we always commenced with cesium alum, and as that is the cheapest and most available salt to begin with, we will give all the details of the method that we finally found to be the best. The cesium alum should be first converted into cesium sulphate. It is not advisable to convert it directly into cesium hydroxide on account of the fact that too much water is required to dissolve the cesium alum, and also because cesium hydroxide absorbs carbon dioxide very rapidly. In order to convert cesium alum into cesium sulphate the following reaction can be used:

$$2CsAl(SO_4)_2.12H_2O + 3Ba(OH)_2.8H_2O = Cs_2SO_4 + 2Al(OH)_3 + 3BaSO_4 + 48H_2O.$$

Dissolve the cesium alum in as small a quantity of boiling-water as possible (it is more convenient in all operations connected with cesium to use casseroles rather than dishes or beakers), and in a separate casserole dissolve the crystalline barium hydroxide; when both are in solution, mix the two and filter rapidly with a good pump; a Buchner funnel can be used in this operation to great advantage. The filtrate if slightly alkaline, due to an excess of barium hydroxide, should be treated with carbon dioxide for a few minutes and quickly refiltered. It can now be either evaporated to dryness or crystallized. The next step is to convert the cesium sulphate into cesium hydroxide.

$$Cs_2SO_4 + Ba(OH)_2.8H_2O = 2CsOH + BaSO_4 + 8H_2O.$$

The sulphate is quite soluble in hot water, and as small a quantity of the solvent as possible should be used. The barium hydroxide should also be separately dissolved in a very small quantity of water. When both are in solution mix and filter with a suction-pump and Buchner funnel. The filtrate is

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[1] *Proc. Russ. Phys. Chem. Ges.*, *1894*.

rapidly evaporated to dryness in a silver crucible and then fused; it should now be poured into a silver dish so that it will make a thin brittle cake of cesium hydroxide, which must not be exposed to the air longer than is absolutely necessary; it is quickly broken, transferred to a warm dry bottle, and weighed; then put into a hot porcelain mortar, broken into small pieces about half the size of a pea, and mixed with one-half its weight of magnesium powder (the magnesium powder must be previously heated in a current of hydrogen to get rid of the fat with which it is always mixed); the mixture is then quickly dropped into a clean, dry, rust-free malleable iron tube of the following dimensions: one meter long, fifteen mm. diameter, three mm. thick, and fifteen cm. from the end it is bent to an angle of about 125°. In order to keep the mixture in the tube a small bundle of clean piano wire irregularly twisted together is forced into the tube down the long part to the angle, before dropping in the mixture. In filling the tube it is best held inclined. The tube is now laid in a slightly inclined combustion furnace, to aid the flow of the liquid metal and quickly connected to a Kipp hydrogen generator. The hydrogen must be passed through permanganate solution in order to oxidize hydrogen arsenide and then thoroughly dried by sulphuric acid and phosphoric anhydride; the bent end of the tube is immersed in liquid paraffin to the depth of about two cm. It is advisable to have the paraffin in a casserole about seven and one-half cm. in diameter. To begin the distillation, light the burner farthest away from the mixture (the tube should never be more than one-third full), and allow hydrogen to pass through at the rate of about forty bubbles per minute. When the temperature has risen as high as one burner can produce, light the next but do not turn on full pressure immediately; this process must be continued, burner by burner, until reaction begins. This is readily marked by an increase in the speed of bubbling through the paraffin. If the bubbles come faster than 80–100 per minute, turn out the last-lighted burner and remove the tile over the tube. Bubbling will now gradually cease, due to the probable formation of hydride of cesium, decomposed at high temperatures; consequently the hydrogen pressure must be increased until gas comes through the paraffin. When the back suction is relieved the hydrogen stream can be restored to its normal rate. This operation must be continued until all the burners are lighted and the temperature is full red. The angle piece of the tube, which should be as close to the furnace as possible, is now heated by a powerful Bunsen burner, and constantly struck with a piece of iron. The metallic cesium which has distilled into this part of the apparatus, will be liquefied, and will trickle down under the paraffin, collecting in silvery drops. The cesium comes out of the tube at the very end of the process and not before. If the foregoing directions are closely followed the whole operation can be accomplished in four hours without the slightest difficulty or danger. Explosions only occur when the tube is heated too rapidly and not sufficient attention paid to the pressure regulation. It is evident from the result of these experiments that Winkler was mistaken in stating that it is impossible to obtain cesium from its compounds by the aid of magnesium. We made cesium in quantity by our method and are now studying its physical properties.

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THE OXIDATION OF FORMIC ALDEHYDE BY HYDROGEN PEROXIDE.[1]

BY J. H. KASTLE AND A. S. LOEVENHART.

Received October 24, 1898.

A FEW preliminary experiments seemed to indicate that the oxidation of formic aldehyde by hydrogen peroxide, could be easily and certainly followed by determining the quantities of formic acid produced as the result of the oxidation, by standard alkali, using phenolphthalein as the indicator. A study of this oxidation was therefore undertaken. A number of oxidations, involving hydrogen peroxide as the oxidizing agent, have been studied. The work of Magnanini[2] and that of Harcourt[3] and Essen on the effect of this substance on hydriodic acid, under different physical and chemical conditions, is important and interesting in this connection. A study of the oxidation of gaseous acetic aldehyde by oxygen gas was undertaken a short

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[1] Read before the Boston meeting of the American Association for the Advancement of Science, August 25, 1898.

[2] *Gaz. chim. ital.*, 20, 377, *1890*.

[3] *Phil. Trans.*, *1867*, 157, 20, 460 and *Phil. Trans.*, *1895*, 186, 817, 895.

time ago by van't Hoff[1] with the view of determining the relation of the pressure under which the oxygen acts to the rate of oxidation. He found the oxidation to proceed with convenient speed at 20° C. and observed that the action was affected by light. His results showed the velocity of the oxidation to be proportional to the pressure of the aldehyde vapor, and to the square root of the pressure of the oxygen. So far as we have been able to discover, this is the only case of the kind that has ever been investigated. It seemed to us, therefore, all the more important to undertake the study of the oxidation of formic aldehyde by hydrogen peroxide in aqueous solution. Marchand's hydrogen peroxide and Schering's formaldehyde were used in the investigation. The solution of formaldehyde was standardized by heating with potassium hydroxide, and the hydrogen peroxide by means of a standard solution of potassium permanganate. The peroxide was always standardized immediately before using, in order to correct any change in strength that it might have undergone. Normal solutions of formaldehyde and peroxide were employed in equivalent volumes, so that in all cases, not stated to the contrary, the reaction was studied at half-normal dilution.

The effect of temperature was first investigated. Our preliminary experiments indicated that the reaction proceeded with extreme slowness at ordinary temperatures, but with great velocity at the temperature of boiling water. It was therefore decided to conduct a series of experiments at each of the following temperatures; *viz.*, 20° C., 26° C., 40° C., 50° C., 60° C., 70° C., 80° C., 90° C., and 98° C. It should be said further that these several series were tried in dark, it having been observed that light exerted an accelerating influence on the progress of the reaction. In each of these experiments five cc. of normal formaldehyde was placed in a test-tube, together with five cc. of normal hydrogen peroxide; the tube was then sealed and placed in a water-bath, which was maintained constant at the temperature desired. The tube was then exposed to certain temperatures for different intervals of time, at the end of which they were plunged into cold water, opened and their contents titrated with fifth-normal potassium hydroxide. The coefficients of

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[1] Etudes de Dynamique Chimique, *1895*, p. 79.

velocity were then calculated from the results by the equation for bimolecular reactions:

$$\frac{1}{\theta}\left(\frac{x}{A-x}\right)\frac{1}{A} = K$$

where θ represents time in minutes, A the initial amount of the substance present, x the amount of substances changed, and K is the constant which measures the velocity of the reaction.

The following are the tabulated results of the series together with the calculated coefficients of velocity:

SERIES AT 40°.

Time. Minutes.	Fifth-normal potassium hydroxide neutralized. cc.	Decomposed. Per cent.	Coefficient of velocity.
30	0.29	1.16	0.0000157
60	0.63	2.52	0.0000172
90	0.97	3.88	0.0000179
120	1.32	5.28	0.0000185
150	1.71	6.84	0.0000196
180	2.00	8.00	0.0000193
222½	2.48	9.92	0.0000198
240	2.65	10.60	0.0000198
270	3.10	12.40	0.0000208
300	3.47	13.88	0.0000201
		Average coefficient of velocity,	0.0000189

SERIES AT 50°.

Time. Minutes.	Fifth-normal potassium hydroxide. cc.	Decomposed. Per cent.	K.
30	1.10	4.40	0.0000614
60	2.13	8.52	0.0000621
90	3.30	13.20	0.0000676
120	4.45	17.80	0.0000722
150	5.20	20.80	0.0000700
180	5.85	23.40	0.0000679
210	6.90	27.60	0.0000726
240	7.63	30.52	0.0000732
270	8.10	32.40	0.0000710
300	9.00	36.00	0.0000750
		Average coefficient of velocity,	0.0000693

SERIES AT 60°.

Time. Minutes.	Fifth-normal potassium hydroxide. cc.	Decomposed. Per cent.	K.
75	7.75	31.00	0.000240
90	8.95	35.80	0.000248
105	9.75	39.00	0.000244
120	10.75	43.00	0.000251
135	11.45	45.80	0.000250
150	11.90	46.70	0.000244
165	12.55	50.20	0.000244
180	13.20	52.80	0.000249
195	14.15	56.60	0.000268
210	14.35	57.40	0.000257
225	14.70	58.80	0.000254
240	15.00	60.00	0.000250
255	15.5	62.00	0.000256
270	15.90	63.60	0.000259
285	16.15	64.60	0.000255
300	16.23	64.92	0.000247
		Average coefficient of velocity,	0.000251

SERIES AT 70°.

Time. Minutes.	Fifth-normal potassium hydroxide. cc.	Decomposed. Per cent.	K.
15	5.15	20.60	0.000691
45	11.25	45.00	0.000727
60	13.20	52.80	0.000746
75	14.80	59.20	0.000774
90	15.65	62.60	0.000744
105	16.65	66.60	0.000760
120	17.45	69.80	0.000770
135	17.65	70.60	0.000711
150	17.75	71.00	0.000653
165	19.20	76.80	0.000802
180	19.55	78.20	0.000799
195	19.95	79.80	0.000772
210	20.65	82.60	0.000754
225	20.65	82.60	0.000704
240	20.65	82.60	0.000660
		Average coefficient of velocity,	0.000711

SERIES AT 80°.

Time. Minutes.	Fifth-normal potassium hydroxide. cc.	Decomposed. Per cent.	K.
10	10.15	40.60	0.00273
20	13.85	59.40	0.00248
35	16.93	67.72	0.00240
50	19.05	76.20	0.00256
60	19.85	79.40	0.00257
80	20.60	82.40	0.00234
100	21.60	86.40	0.00254
120	21.95	87.80	0.00240
150	22.80	91.20	0.00276
		Average coefficient of velocity,	0.00253

SERIES AT 90°.

Time. Minutes.	Fifth-normal potassium hydroxide. cc.	Decomposed. Per cent.	K.
5	12.10	48.40	0.00750
15	17.20	68.80	0.00590
20	18.54	74.16	0.00555
30	20.60	82.40	0.00625
50	21.70	86.80	0.00525
60	22.80	91.20	0.00690
		Average coefficient of velocity,	0.00625

It was noted that considerable pressure was developed in the tubes up to this temperature, *viz.*, 90° C., owing to the fact that the hydrogen peroxide liberates its oxygen more rapidly than it is capable of acting on the formaldehyde; but at this temperature the pressure almost disappears indicating that the peroxide acts on the formic aldehyde at this temperature very nearly as rapidly as it is capable of liberating its oxygen.

SERIES AT 98°.

Time. Minutes.	Fifth-normal potassium hydroxide. cc.	Decomposed. Per cent.	K.
10	18.90	75.60	0.0124
15	20.50	82.00	0.0122
20	21.60	86.40	0.0127
30	22.30	89.20	0.0110
45	23.06	92.24	0.0106
60	23.50	94.00	0.0105
		Average coefficient of velocity,	0.0116

A few experiments were tried at lower temperatures; at 20° the coefficient of velocity was found to be approximately 0.000000855, and at 26°, 0.00000199.

In harmony with the theory of bimolecular reactions the coefficients of velocity of this reaction, for any particular temperature, approach a constant value. This is especially true of the values obtained for 50° C., 60° C., and 70° C., and in all cases they are probably sufficiently n value to justify one in assuming that a very close approximation to the tr In considering these results, howeve borne in mind that there are several perimental error which can scarcel One of these is due to the fact that takes place so rapidly in alkaline so is difficult oftentimes to make sure of tion. Then, again, a small amount of peroxide decomposes into water an this liberated oxygen acts far less r formaldehyde than that contained i molecule. A third factor which n slight departure of the observed valu stant is that the formic acid produc dation very slightly accelerates the effect of temperature on the course under consideration is very clearly curve. On this, temperatures have been laid off on the axis of abscissas, the ordinates being the average coefficients of velocity of the reaction, multiplied, for convenience, by 3333⅓. The enormous but regular effect of temperature on the velocity of this reaction is clearly shown by this curve. From 20° to 40° C. it will be observed that the curve is nearly coincident with the axis of *x*; then, very slowly at first, but very rapidly later on, it begins to diverge from it, until at 90° to 98° C. it is almost perpendicular to it, indicating that we would not have to raise the temperature

Ordinates = Average
Coefficients of velocity × 3333⅓.

of the system any very great deal in order to make the change practically instantaneous.

The effect of light on the progress of reaction has also been investigated. The fact that hydrogen peroxide is more unstable in the light than in the dark would naturally lead to the supposition that light would probably accelerate the oxidation under discussion. A few preliminary experiments indicated that such was really the case. Two tubes, each containing ten cc. normal formic aldehyde and ten cc. normal hydrogen peroxide, were kept at 20° C., one in the sunlight and one in the dark, for five and one-half hours. The tube in the dark showed a decomposition of seven-tenths per cent., whereas that in the light gave four per cent. decomposition. It was therefore decided to carry through several series in the direct sunlight at the same temperature as those which were tried in the dark, and under conditions as nearly identical as possible. The extremely variable character of even bright sunlight is capable of causing variations in the velocity of the reaction in the same series, so that for the several series in the sunlight the values of K show greater deviation from a constant value than those obtained for the same series in the dark. In light at 20° the coefficient of velocity was found to be 0.00000505 and at 26°, 0.00000629.

SERIES IN DIRECT SUNLIGHT AT 40° C.

Time. Minutes.	Fifth-normal potassium hydroxide. cc.	Decomposed. Per cent.	K.
45	0.75	3.00	0.0000275
60	1.00	4.00	0.0000278
90	1.85	7.40	0.0000355
120	2.85	11.40	0.0000429
150	3.30	13.20	0.0000401
180	4.40	17.60	0.0000475
240	5.10	20.40	0.0000427

Average coefficient of velocity 0.0000378, thus showing an increase of 100 per cent. over the average coefficient of velocity in the dark at the same temperature.

Series in Direct Sunlight at 50° C.

Time. Minutes.	Fifth-normal potassium hydroxide. cc.	Decomposed. Per cent.	K.
60	3.35	13.40	0.000104
75	4.05	16.20	0.000103
90	4.85	19.40	0.000107
105	5.45	21.80	0.000106
120	6.95	27.80	0.000128
135	7.15	28.60	0.000119
150	7.70	30.80	0.000119
165	8.65	34.60	0.000128
180	10.35	41.40	0.000156
195	11.05	44.20	0.000162
215	11.78	47.12	0.000168
233	11.78	47.12	0.000153
		Average coefficient of velocity,	0.000129

Series in Direct Sunlight at 60° C.

Time. Minutes.	Fifth-normal potassium hydroxide. cc.	Decomposed. Per cent.	K.
30	3.85	15.40	0.000243
45	5.30	21.20	0.000239
60	6.65	26.60	0.000242
75	8.05	32.20	0.000253
90	8.85	39.40	0.000288
105	10.75	43.00	0.000287
120	11.53	46.12	0.000285
135	12.35	49.40	0.000290
150	13.39	53.56	0.000308
165	13.63	54.52	0.000291
180	15.01	60.04	0.000336
195	15.85	63.40	0.000356
216	16.35	65.40	0.000350
225	16.40	65.60	0.000339
270	18.20	72.80	0.000397
300	19.05	76.20	0.000427
		Average coefficient of velocity,	0.000308

Series in Direct Sunlight at 70° C.

Time. Minutes.	Fifth-normal potassium hydroxide. cc.	Decomposed. Per cent.	K.
45	5.95	47.60	0.000805
90	7.95	63.60	0.000777
135	9.45	75.60	0.000918
180	10.15	81.20	0.000959
		Average coefficient of velocity,	0.000865

SERIES IN DIRECT SUNLIGHT AT 80° C.

Time. Minutes.	Fifth-normal potassium hydroxide. cc.	Decomposed. Per cent.	K.
20	13.85	55.40	0.00248
35	17.10	68.40	0.00247
50	18.90	75.60	0.00248
60	20.00	80.00	0.00267
80	21.31	85.20	0.00288
100	21.95	87.80	0.00288
120	21.95	87.80	0.00240
150	23.00	92.00	0.00307
225	23.20	92.80	0.00228
		Average coefficient of velocity,	0.00262

SERIES IN DIRECT SUNLIGHT AT 90° C.

Time. Minutes.	Fifth-normal potassium hydroxide. cc.	Decomposed. Per cent.	K.
15	17.30	69.20	0.00595
20	19.30	77.20	0.00675
30	20.40	81.60	0.00590
55	22.10	88.40	0.00555
75	23.20	92.80	0.00690
		Average coefficient of velocity,	0.00621

The results, like those obtained in the dark, can best be represented graphically by the curve, the abscissas of which represent the temperatures and the ordinates the average coefficients of velocity multiplied by 3333⅓. From this it will be seen, at a glance that for certain temperatures, at least, light exerts an accelerating influence on the progress of the reaction. The point of chief interest, however, is that the effect of light is different for different temperatures. What it is at 0° C. we have not yet had an opportunity to determine, in consequence of the extreme slowness of the change. Generally, however, it will be seen that the accelerating effect of light is greatest for low temperatures, gradually diminishing with increasing temperature until at a temperature just a little below 90° C., the curves intersect and become identical for light and dark. When we compare the velocity of this reaction at 20° C. and 40° C. and observe the great falling off in the rate of change it can be fairly surmised that somewhere, probably not very far removed from 0° C. on either side, the reaction would cease altogether, both in light and dark. It would seem then that the accelerating influence of light is possible only between certain rather narrow limits of temperature. That such is the case seems to have been proved also, for reactions other than the one under discussion. Amato[1] has shown, for example, that if a mixture of hydrogen and chlorine be cooled to —12° C. it could be exposed to direct sunlight for hours without any combination taking place. It is further conceivable with reference to this particular reaction that at very high temperatures it would take place so rapidly that light would be without effect on the change. In the same way Beatty[2] and one of us have shown that while light cannot cause the combination of hydrogen and bromine at ordinary temperatures, it greatly accelerates their combination at 197° C.; at still higher temperatures it is quite possible that its effect on this system would be lost. The chemical action of light is at best so little understood that considerable interest attaches to these results which would seem to support the view that a certain amount of the energy of the light actually enters into, and becomes a part of, the system undergoing change. Below a certain temperature the heat and light energy together might be insufficient to cause the change. At temperatures at which the given reaction becomes possible, however, light would accelerate, for the reason that the increment of energy furnished by it would be a measurable amount of the entire quantity of energy present. At very high temperatures this increment of light energy would become so small, as compared with the increased heat energy of the system, as to cause the effect of the light to disappear altogether.

ON THE EFFECT OF ACIDS AND BASES ON THE OXIDATION.

It has been announced as a general proposition that "all oxidation and reduction processes are accelerated by the presence of free acids, in proportion to their coefficients of affinity."[3] It was therefore deemed desirable to try the effect of acids on this particular case. In order to do this, three series of experiments were carried through at 50° C.: one with hydrochloric

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[1] *Gazz. chim. ital.*, 14, 57.

[2] *Am. Chem. J.*, 20, 159.

[3] Schlundt and Warder: *Am. Chem. J.*, 18, p. 31.

acid, one with formic acid, and one with water alone. In each experiment five cc. normal formaldehyde, five cc. normal hydrogen peroxide, and five cc. of water or the acid were mixed, placed in sealed tubes and kept at 50° C. for the several desired intervals of time. The following series were carried through:

(1) With hydrochloric acid	0.0000754
(2) With formic acid	0.0000705
(3) With water	0.0000670

HYDROCHLORIC ACID SERIES.

Mixture: Five cc. normal hydrogen peroxide, five cc. normal formaldehyde, and five cc. normal hydrochloric acid.

Time. Minutes.	Fifth-normal potassium hydroxide. cc.	Decomposed. Per cent.	K.
60	2.25	9.00	0.0000659
90	3.53	14.12	0.0000737
120	4.33	17.32	0.0000698
180	6.55	26.20	0.0000789
210	7.45	29.80	0.0000809
240	8.00	32.00	0.0000784
270	8.75	35.00	0.0000799
		Average coefficient of velocity,	0.0000754

FORMIC ACID SERIES.

Mixture: Five cc. normal hydrogen peroxide, five cc. normal formaldehyde, and five cc. normal formic acid.

Time. Minutes.	Fifth-normal potassium hydroxide. cc.	Decomposed. Per cent.	K.
60	2.10	8.40	0.0000611
90	3.15	12.60	0.0000641
120	4.40	17.60	0.0000745
150	5.08	20.32	0.0000680
180	6.20	24.80	0.0000733
210	6.95	27.80	0.0000733
240	7.80	31.20	0.0000756
270	8.40	33.60	0.0000750
		Average coefficient of velocity,	0.0000705

SERIES WITH WATER.

Mixture : Five cc. normal hydrogen peroxide, five cc. normal formaldehyde, and five cc. water.

Time. Minutes.	Fifth-normal potassium hydroxide. cc.	Decomposed. Per cent.	K.
60	2.10	8.4	0.0000611
90	3.20	12.8	0.0000652
120	4.07	16.28	0.0000648
150	4.90	19.60	0.0000650
180	5.88	23.52	0.0000680
210	6.92	27.68	0.0000730
240	7.30	29.20	0.0000690
270	8.12	32.48	0.0000712
		Average coefficient of velocity,	0.0000670

It will be observed that the acids caused some acceleration in the rate of change, and that hydrochloric acid caused a greater acceleration than formic. It is not by any means so marked as it is in certain other oxidations that have been studied, a fact that can doubtless best be explained by assuming that the accelerative tendency of the acid is counterbalanced to some extent by an increased stability in the hydrogen peroxide, which latter is also brought about in some way by the acid. The acceleration produced by formic acid, however, is probably sufficiently great to account for the increase in velocity usually observed at the end of a long series. The formic acid produced during the oxidation would cause the reaction to proceed more rapidly towards the end. The effect of bases on the rapidity of the oxidation is certainly most remarkable. In consequence of the rapidity of the oxidation, all of our experiments with bases have been conducted at ordinary temperatures. In each experiment five cc. normal formaldehyde and five cc. normal hydrogen peroxide were placed in a flask, and a quantity of half-normal base then added—equivalent to the amount of formic acid produced by the oxidation, and from the time of adding the solution of the base the duration of the experiment was counted. At the end of a given time an amount of normal hydrochloric acid was added—equivalent to the original amount of base present—and the solution was then titrated back with standard caustic potash, using phenolphthalein as an indicator. During the progress of the reaction with bases, considerable effervescence occurred, due to escaping oxygen. The reaction is affected by light, and slight changes in temperatures also produced quite a noticeable effect on the rate of change.

Caustic potash, caustic soda, and ammonia were first compared as to their effect on the reaction, each active substance reacting in fourth-normal solution. The results obtained are given in the following table.

TABLE I.

Time. Minutes.	Potassium hydroxide. Per cent.	Sodium hydroxide. Per cent.	Ammonium hydroxide. Per cent.
2	48.4	46.0	15.0
4	62.5	61.0	24.0
6	70.0	69.0	31.0
8	76.5	74.0	37.0
10	78.0	77.0	40.0
15	87.0	88.0	44.0
20	99.5	99.0	49.0
25	....	....	54.4
35	....	....	56.0
83	....	....	69.0
1350	....	....	86.4

These results are of interest, first, as showing the remarkable acceleration produced by alkalies on the progress of this reaction. Few, if any, attempts have been made to follow any reaction occurring with such rapidity. It will be seen, further, that caustic potash and soda are practically the same in their effect, and that both act much more vigorously than ammonia. This is in harmony with our present knowledge respecting the activity of these bases. The action of barium hydroxide on this oxidation was also tried. Owing to lack of solubility, it could not be compared with these bases at the dilution at which the above comparisons were made. As concentrated a solution as possible of this base was made (which happened to be nearly third-normal), 14.5 cc. being equivalent to five cc. normal hydrochloric acid. This was compared with caustic potash of exactly the same strength, so that in these experiments the active substances were present in about fifth-normal solution. In each experiment five cc. normal formic aldehyde, five cc. hydrogen peroxide, and 14.5 cc. of the given base were employed. The following results were obtained:

TABLE II.

Time. Minutes.	Potassium hydroxide. Per cent.	Barium hydroxide. Per cent.
2	43.0	53.4
4	57.0	67.4
6	63.0	68.0
8	66.4	71.0
10	72.0	74.0
15	74.4	78.0
20	82.4	81.0
25	84.4	82.4
30	85.0	86.0

In the last five experiments of this series it will be observed that caustic potash and barium hydroxide are exerting practically the same effect on the rate of oxidation. At first, however, the barium hydroxide acts more rapidly. In the experiments with barium hydroxide at this dilution we always obtained a white precipitate, probably barium dioxide, and this may have altered the conditions to such an extent as to cause this difference in the effect of these two bases. It is our intention to study the effect of bases at greater dilutions, so as to include lime and strontium hydroxide in the comparison. The great acceleration produced by bases on this oxidation has suggested another important line of work, in which only the merest beginning has as yet been made. This is with reference to the hydrolysis of salts. It was thought that this reaction might furnish us with a very delicate method for the measurement of the hydrolysis of alkaline salts. It has been found, for example, that while common salt is without influence on rate of change at 50° C., it is greatly accelerated by sodium acetate. We have not yet had an opportunity to make any thorough study of this phase of the reaction, but the following comparisons of the action of hundredth-normal potassium hydroxide and normal sodium acetate is interesting, as showing the possibilities of this method in measuring the hydrolysis of salts.

Two series of experiments were tried, in the dark, at 60° C. In series No. 1, one cc. normal formaldehyde was mixed with one cc. normal hydrogen peroxide, one cc. hundredth-normal caustic potash, and seven cc. of water in each experiment. In series No. 2, exactly the same quantities of substances were used, except that instead of hundredth-normal caustic potash, one cc. normal sodium acetate was employed. The coefficients of velocity obtained in the two series are given in Table III.

TABLE III.

Time. Minutes.	Series No. 1, potassium hydroxide.	Series No. 2, normal sodium acetate.
68	0.000141	0.000218
90	0.000141	0.000209
120	0.000156	0.000231
Average	0.000146	0.000219

These results would indicate that at this temperature and dilution, sodium acetate is hydrolyzed to the extent of over one per cent. This number is probably not far from the truth. A more thorough study especially of this last phase of the reaction will soon be undertaken.

STATE COLLEGE OF KENTUCKY,
LEXINGTON, July, 1898.

UPON THE ACTION OF SULPHURIC ACID ON THYMOL.[1]

[THIRD PAPER.]

BY JAMES H. STEBBINS.

Received December 15, 1898.

MY motive in taking up this subject again, is for the purpose of clearing up certain doubts which had arisen in my mind, in connection with my previous experiments.[2]

Photomicrographic examinations of the products previously obtained showed so many different forms of crystallization, that I was led to believe that by the treatment of thymol with 66° sulphuric acid, at steam-bath temperature, possibly several isomeric acids are formed.

To gain more light upon this question, therefore the following experiments were made :

Sixty grams of powdered thymol were heated in a beaker on the water-bath, under constant stirring, with fifty grams of 66° sulphuric acid, until the mixture solidified to a crystalline mass, which occurs after nine to ten minutes' heating.

As previously noted, a small quantity of a clear, oily-looking liquid separates, on pressing, from the crystalline cake. This, on being poured off into a beaker, solidifies on cooling to a mass of minute white needles.

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[1] Read by title before the New York meeting of the American Chemical Society, December 28, 1898.

[2] This Journal, 3, 103, 110, (*1881*).

This product was marked "A" and set aside for further examination.

The main crystalline mass or product "B", resulting from the action of sulphuric acid on thymol, was dissolved in hot water and filtered from a small quantity of a dark oily-looking liquid which floated on its surface and which appeared to be thymol. The filtrate was then neutralized with barium carbonate, filtered from the barium sulphate, and concentrated on the water-bath, till crystals began to show on the surface of the liquid. It was then set aside to crystallize.

A large crop of white flat-sided prisms was obtained. These were sucked as free from mother-liquid as possible, by the aid of a suction-pump and, after pressing between folds of filter-paper, were redissolved in a small quantity of hot water and the solution set aside to crystallize.

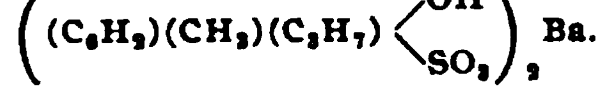
A barium salt "B" is thus obtained, which contains water of crystallization, a part of which is lost on exposure to the air, or over sulphuric acid, and the whole of it is driven off under partial decomposition of the salt, when the latter is heated to 100°.

One of the peculiarities of this salt, is the fact that it crystallizes from water in several crystalline forms, according as to whether the crystallization is allowed to take place gradually or rapidly.

By the slow evaporation of its aqueous solution, it is obtained in the shape of rhombic plates or prisms (Figs. 1 and 2). By a more rapid evaporation of the aqueous solution, it may be obtained in striated crystals, radiating from a common center (Fig. 3).

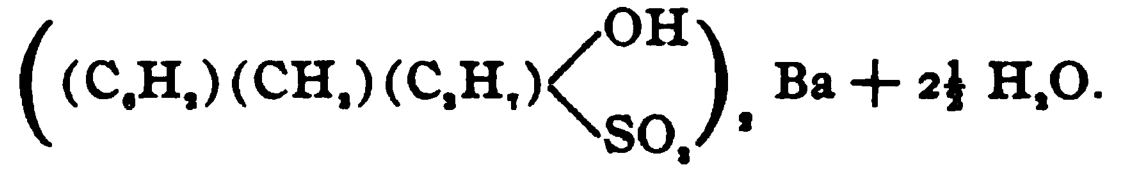
0.9324 gram substance, dried at 100°, lost 0.0724 gram water, equal to 2.55 molecules,—or in round numbers 2½ molecules of water of crystallization.

0.760 gram substance, dried at 100°, gave 0.2961 gram barium sulphate.



	Theory for $\left((C_6H_2)(CH_3)(C_3H_7)\begin{smallmatrix}OH\\SO_3\end{smallmatrix}\right)_2 Ba.$	Found.
Ba	23.02	22.90
2½ H_2O	7.03	7.84

Therefore the barium salt of what I will temporarily call alphathymolsulphonic acid has the following empyrical formula:



$$\left((C_6H_2)(CH_3)(C_3H_7)\left\langle{OH \atop SO_3}\right.\right)_2 Ba + 2\tfrac{1}{2}\ H_2O.$$

A comparison of my product with the barium salt of the alphathymolsulphonic acid, described by Engelhardt and Latschinoff,[1] shows that they are identical in all respects, save the water of crystallization. Engelhardt and Latschinoff claim two molecules of water of crystallization for their barium salt, while I find that mine crystallizes with two and one-half molecules of water of crystallization.

The barium salt of alphathymolsulphonic acid, above described, is very easily soluble in water and alcohol, from which, as already stated, it crystallizes in various forms, dependent upon the manner in which crystallization is brought about.

FREE ALPHATHYMOLSULPHONIC ACID.

In one of my previous papers[2] a method was described for obtaining this compound from its lead salt, by precipitating the lead with hydrogen sulphide. It may, however, also be prepared from its barium salt, by treating the latter with sufficient sulphuric acid to precipitate out all the barium present as barium sulphate. The latter is then collected upon a filter, washed, and the filtrate concentrated to the consistency of a sirup on the water-bath. On standing, the free thymolsulphonic acid crystallizes out, in the shape of rhombic plates or tables (Fig. 4). If, however, the sirup be agitated, or better still, if the bottom of the crystallizing dish be scratched with a glass rod, the sulphonic acid will be obtained in the shape of rhombic prisms grouped together fern-shaped and may at times be accompanied by some rhombic plates (Fig. 5). It is freely soluble in both hot and cold water and, as previously noted, was found to melt at 91°–92° C. Since in my previous papers no attempt was made to determine the true constitution of this interesting body, it was thought that a little more light upon the subject would not only be interesting but desirable. To gain this information, it was decided to submit the sulphonic acid to the action of oxidizing agents, with the view, if possible, of converting it into a

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[1] *Ztschr. Chem.*, *1869*, p. 44.

[2] This Journal, 3, 111 (*1881*).

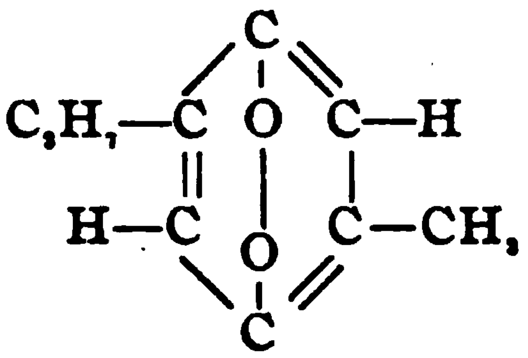
FIG. 2.

FIG. 4

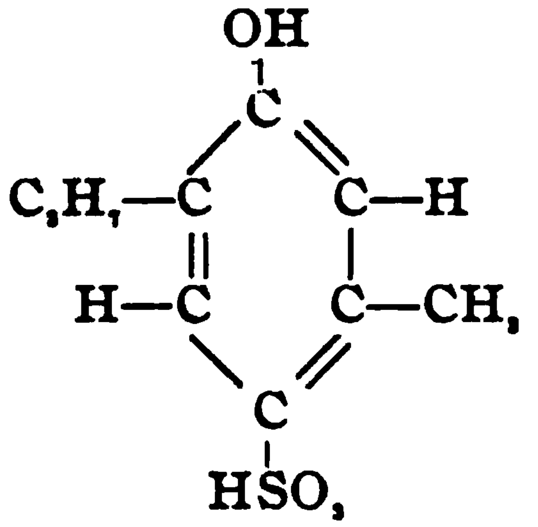
FIG. 6

quinone, and from it determine the true constitution of the thymolsulphonic acid. For this purpose the following experiment was made :

Ten grams of the sodium salt of alphathymolsulphonic acid were dissolved in 100 cc. of water and to the solution was added a solution of thirty grâms potassium bichromate, and ten grams of 66° sulphuric acid in 100 cc. of water. The mixture was now heated under a reflux condenser for about one-half hour and then submitted to steam distillation. A yellow oily liquid of penetrating and peculiar smell, passes over with the steam, and solidifies partly in the condenser and partly in the recipient, to a mass of yellow crystalline leaflets. These after recrystallization from alcohol and water, have the constant melting-point of 45.5°, and unite with hydroxylamine chloride to form a well-characterized oxime. From the above and its general characteristics, it was identified as thymoquinone of the following constitution :



Therefore as in the process of oxidation, the HSO_3 group and OH group are necessarily replaced by the two CO-groups, it follows that the constitution of my thymolsulphonic acid must be represented by the following formula :



That is, the HSO_3 group stands in the para position, in relation to the OH group.

It has also been shown by Ad. Claus,[1] that Engelhardt and Latschinoff's alphathymolsulphonic acid, is a parasulphonic acid, and as my acid is identical with their product, it follows that this is an additional proof of the correctness of the constitutional formula above set forth.

Engelhardt and Latschinoff[2] mention two other isomeric thymolsulphonic acids, which they obtained simultaneously with the para acid, and which they designate as the β- and γ-acid. These are separated from the para acid by the difference in solubility of their potassium salts, the potassium salt of the para acid being much more freely soluble than the potassium salt of the β-acid (according to Claus, the β-acid is the orthosulphonic acid and the γ-acid, a mixture of para and disulphonic acids).

It therefore seemed possible that by my mode of operating, isomeric acids might likewise be formed and to settle this question the following experiment was made :

The mother-liquor separated from the barium salt of thymolparasulphonic acid, was diluted with water, heated to boiling and treated with sufficient potassium carbonate, to precipitate all the barium present, as barium carbonate. The latter was collected upon the filter, washed with hot water and the filtrate concentrated to a small volume by evaporation ; no crystals of a difficultly soluble potassim salt separated on cooling, hence Engelhardt and Latschinoff's β-sulphonic acid or thymolorthosulphonic acid was absent. As a further evidence of the absence of the ortho acid, the above solution was evaporated to dryness, and the dry residue dissolved in ninety per cent. alcohol, in which it is very soluble. On cooling no separation of a difficultly soluble potassium salt occurred and it is only after evaporating the alcoholic solution to the consistency of a sirup and allowing the latter to cool, that I was finally able to obtain the potassium salt in a crystalline form. The product thus obtained crystallizes from alcohol, in rhombic crystals which are freely soluble both in alcohol and water. From water it crystallizes in flat-sided needles. A comparison of this salt, with the potassium salt of thymolparasulphonic acid described by Engelhardt and Latschinoff, shows that they are identical.

[1] *J. prakt. Chem.*, 43, 334-355.

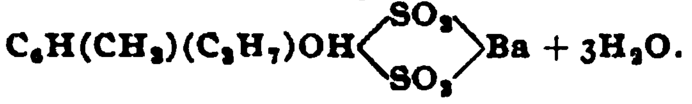
[2] *Loc. cit.*

The oily product "A" referred to in the early part of this paper, as being formed in small quantity by the action of sulphuric acid on thymol, at 100°, crystallizes on cooling to a white crystalline mass which, when viewed under the microscope, is seen to be composed of a multitude of little white needles (Fig. 6). The product was dissolved in cold water, heated to boiling, and neutralized with barium carbonate. The barium sulphate formed was collected upon a filter, washed with hot water, and the filtrate concentrated to a small volume on the water-bath.

After several weeks' standing a barium salt was obtained which crystallized in long white needles, some of which were two or three centimeters long. The yield of this product was, however, very small, hardly enough for analysis being obtainable. It is exceedingly soluble in water and for this reason is difficult to obtain in a crystalline form. It crystallizes with water of crystallization.

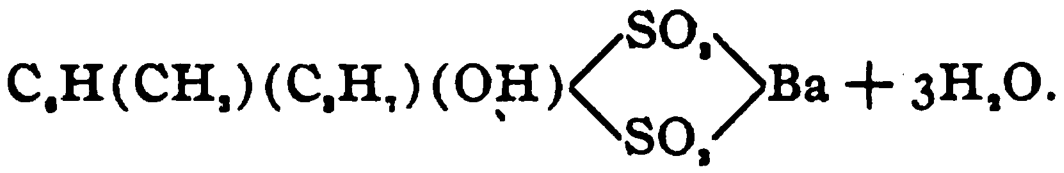
0.3399 gram salt, dried at 100°, lost 11.29 per cent. water.

0.3012 gram salt, dried at 100°, gave 0.1472 gram barium sulphate.



	Theory for $C_6H(CH_3)(C_3H_7)OH\left\langle\begin{matrix}SO_3\\SO_3\end{matrix}\right\rangle Ba + 3H_2O.$	Found.
H_2O	13.53	11.29
Ba	30.78	28.71

From the above it is evident that the barium salt analyzed was not pure, but as the figures obtained agree much better with the theory for a disulphonid acid than anything else coupled with the great solubility of the barium salt, I am inclined to believe that what I had in hand, was a barium salt of thymoldisulphonic acid, which is probably represented by the following formula:



$$C_6H(CH_3)(C_3H_7)(OH)\left\langle\begin{matrix}SO_3\\SO_3\end{matrix}\right\rangle Ba + 3H_2O.$$

Owing to the small quantity of material at my disposal, a more thorough examination of this salt was impossible.

To recapitulate, it will therefore be seen that the only two products formed by the action of 66° sulphuric acid on thymol, at the temperature of boiling water, are thymolparasulphonic acid and thymoldisulphonic acid, of which the former constitutes by far the greater portion, while the latter product is only obtained in very small quantity.

MOLECULAR WEIGHTS OF LIQUIDS, III.

BY CLARENCE L. SPEYERS.

Received December 17, 1898.

A SHORT time ago, I published two papers[1] on this subject, using the equation

$$\frac{n_1}{n_1+n_2}=\frac{p-p'}{p},$$

to determine the molecular weights of liquids in homogeneous liquid mixtures. Recently some more measurements of vapor-pressures of solutions have been published[2] to which measurements this equation can be applied.

Using the notation and arrangements of the preceding paper, we get the following two tables:

CCl$_4$ AND C$_6$H$_6$ (50°).

CCl$_4$ pct. mols.	C$_6$H$_6$ pct. mols.	v. p. CCl$_4$ (310.2).	v. p. C$_6$H$_6$ (270.9).	Mol. wt. CCl$_4$.	m/m_0 CCl$_4$.	Mol. wt. C$_6$H$_6$.	m/m_0 C$_6$H$_6$.
10	90	34.0	242.4	148.4	0.97	81.2	1.0
20	80	67.0	215.0	149.3	0.97	85.7	1.1
30	70	98.2	190.0	155.7	1.0	84.0	1.1
40	60	128.6	166.0	162.9	1.1	82.5	1.1
50	50	157.4	140.0	164.9	1.1	79.9	1.0
60	40	187.5	113.0	165.4	1.1	79.0	1.0
70	30	217.0	87.0	170.0	1.1	77.2	1.0
80	20	247.0	60.0	175.2	1.1	75.3	0.96
90	10	279.0	30.6	176.3	1.1	75.8	0.97

CCl$_4$ AND C$_7$H$_8$ (50°).

CCl$_4$ pct. mols.	C$_7$H$_8$ pct. mols.	v. p. CCl$_4$ (310.2).	v. p. C$_7$H$_8$ (93.0).	Mol. wt. CCl$_4$.	m/m_0 CCl$_4$.	Mol. wt. C$_7$H$_8$	m/m_0 C$_7$H$_8$.
10	90	27.2	85.3	188.8	1.2	79.4	0.86
20	80	54.0	77.4	190.2	1.2	77.4	0.84
30	70	82.4	69.1	190.0	1.2	77.4	0.84
40	60	111.4	60.8	188.4	1.2	77.0	0.84
50	50	143.0	52.0	194.5	1.3	78.3	0.85
60	40	175.4	42.7	195.3	1.3	73.9	0.80
70	30	208.2	33.0	195.9	1.3	79.9	0.87
80	20	240.0	22.7	198.1	1.3	77.9	0.85
90	10	274.0	11.8	200.6	1.3	80.3	0.87

The plots corresponding to these tables are given in Fig. 1.

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[1] *Jour. phys. Chem.*, 2, 347, 362 (*1898*).

[2] Lehfeldt: *Phys. Mag.*, 46, 42 (*1898*).

Composition frac mols CCl_4

Fig. 1.

The vapor-pressure plot of benzene indicates a slight association of carbon tetrachloride when the mixture is concentrated with respect to carbon tetrachloride, but a slight dissociation when the mixture is dilute with respect to it. In view of the nature of carbon tetrachloride, I think we should take this to mean that carbon tetrachloride has a normal molecular weight when mixed with benzene.

The vapor-pressure plot of carbon tetrachloride indicates a slight dissociation of benzene when the mixture is concentrated with respect to benzene, but not enough to show an association of the benzene molecules. The very peculiar plot given by Linebarger[1] is not found here.

The vapor-pressure plot of toluene indicates an association of carbon tetrachloride, but as there was no indication of association in the experiments of Linebarger, I think we are to conclude that carbon tetrachloride has a normal molecular weight in toluene.

The vapor-pressure plot of carbon tetrachloride would indicate a slight dissociation of toluene, but this is hardly admissible, as here likewise we must conclude that toluene has a normal molecular weight in carbon tetrachloride, particularly since the experiments of Linebarger point to the same conclusion.

C_2H_5OH AND C_6H_6 (50°).

C_2H_5OH pct. mols.	C_6H_6 pct. mols.	*v. p.* C_2H_5OH (219.5).	*v. p.* C_6H_6 (270.9).	Mol. wt. C_2H_5OH.	m/m_0 C_2H_5OH.	Mol. wt. C_6H_6.	m/m_0 C_6H_6.
10	90	110.0	264.4	205.1	4.4	705.0	9.0
20	80	135.0	256.6	206.3	4.5	498.0	6.4
30	70	151.0	248.0	213.5	4.6	401.0	5.1
40	60	164.0	237.4	217.3	4.7	346.0	4.4
50	50	175.0	225.8	230.6	5.0	307.0	3.9
60	40	185.2	207.6	226.3	4.9	281.0	3.6
70	30	194.0	183.0	223.5	4.9	254.0	3.3
80	20	203.2	146.0	215.2	4.7	240.0	3.1
90	10	211.4	96.4	228.8	5.0	226.0	2.9

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[1] This Journal, 17, 615, 690 (*1895*); Speyers: *J. phys. Chem.*, 2, 347 (*1898*).

C_2H_5OH AND C_7H_8.

C_2H_5OH pct. mols.	C_7H_8 pct. mols.	*v. p.* C_2H_5OH (219.5).	*v. p.* C_7H_8 (93.0).	Mol. wt. C_2H_5OH.	m/m_0 C_2H_5OH.	Mol. wt. C_7H_8.	m/m_0 C_7H_8.
10	90	110.0	86.8	71.6	1.6	831.0	9.0
20	80	135.0	83.0	95.5	2.1	588.0	6.4
30	70	150.6	80.5	127.0	2.8	469.0	5.1
40	60	162.2	77.8	157.0	3.4	390.5	4.2
50	50	169.6	75.2	194.3	4.2	312.7	3.4
60	40	174.4	71.9	235.1	5.1	237.1	2.6
70	30	179.0	66.8	273.7	5.9	174.3	1.9
80	20	187.8	57.3	295.4	6.4	136.2	1.5
90	10	203.6	36.9	272.2	5.9	130.9	1.4

The plots corresponding to these two tables are given in Fig. 2. We see from the vapor-pressure of alcohol that benzene and toluene are polymerized to a remarkable degree in alcohol, and very equally so from a concentration of 100 per cent. gram-molecules of benzene or toluene down to about sixty per cent. gram-molecules benzene or toluene, but from about sixty per cent. gram-molecules of these two liquids down, they are not equally polymerized in alcohol. The vapor-pressure plot of alcohol with toluene runs so as to indicate a normal molecular weight for toluene in alcohol when the mixture is dilute with respect to toluene, but the vapor-pressure plot of alcohol with benzene does not indicate a normal molecular weight for benzene at any dilution.

We see from the vapor-pressure plot of toluene that alcohol is highly polymerized in toluene, but when the concentration of the toluene is high, the molecular weight of the alcohol drops towards a normal value. This corresponds to the behavior of toluene in alcohol.

The vapor-pressure plot of benzene, however, indicates that alcohol is highly polymerized in benzene at all concentrations. This corresponds to the behavior of benzene in alcohol. On the other hand, there is a possibility that alcohol has a normal molecular weight in benzene when the mixture is dilute with respect to alcohol, for there are two observations of the vapor-pressure of benzene at about 125 mm. mercury, which lie very

Composition pct mols. C_2H_5OH

Fig. 2.

close to the diagonal. If these observations are correct, then alcohol would have nearly normal molecular weights at the concentrations corresponding to these observations, but these observations are so different from the other ones that I thought it best to draw the plot as I did.

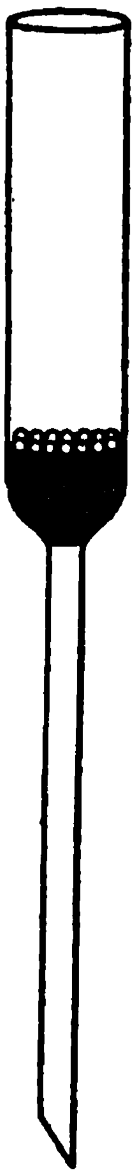
RUTGERS COLLEGE, December 16, 1898.

A NEW FILTERING MEDIUM.[1]

BY GEO. WM. SARGENT AND JNO. KIRK FAUST.

Received November 23, 1898.

FOR the removal of manganese dioxide from the nitric acid in which solution it has been precipitated by potassium chlorate, a glass tube similar to that used for carbon determinations, is recommended. The bottom of this tube is covered first with a small piece of glass wool, then with asbestos. This we used for some time, but were frequently troubled by the precipitate running through, unless a very thick bed of asbestos was made. In this case, the time consumed in filtering was very considerable, due to clogging of the filter by potassium chloride from the large amount of potassium chlorate necessary to oxidize the chromium which was present in considerable quantities in the steels dealt with.



After some experimenting, we adopted the following as giving the most satisfactory results: A carbon filtering tube with a stem five inches long and a body three and one-half inches long and one and one-fourth inches in diameter, is filled one-fourth inch with pewter sand, a small piece of glass wool being used to retain the sand; over this a thin layer of asbestos is formed by pouring in the asbestos shaken up with water and sucking the bed dry. A little hot dilute nitric acid is poured back and forth through the tube several times, when it is ready for use.

When a heavy precipitate is encountered, the bulb from a syringe is used to force air into the tube and drive the liquid through, care being taken to keep the bulb compressed until removed from the tube.

We have found that the quickest and best way to wash the manganese dioxide consists in allowing the nitric acid to run

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[1] Read at the New York meeting of the American Chemical Society, December 28, 1898.

entirely through the filter, then washing all the residue in the beaker into the tube with cold water, and as soon as the filter has drained, washing out the potassium chloride with hot water. The filter and manganese dioxide are blown out into the beaker and the dioxide reduced with ferrous sulphate, etc. The sand and asbestos are recovered and used time and again. The washings and nitric acid filtrate were examined and found free from manganese. In this filtrate the chromium was determined by adding ice and reducing the chromate with ferrous sulphate, etc.[1]

This sand filter was used for the removal of ammonium phosphomolybdate from the solution in which it was precipitated. It was found best to place a few pieces of glass rod upon the asbestos to hold it in position when the solution was first being poured upon the filter. With this device, we have found the freeing of the precipitate and filter of molybdic acid to be more easily and more quickly accomplished than when paper filters were used. The phosphomolybdate has a tendency, as all know, to 'creep,' and, unless the filter is fitted properly to the funnel, to get into the filtrate. This trouble is avoided by the sand filter. To dissolve the precipitate, the ammonia solution is poured through the filter two or three times and finally washed out with hot water. A number of determinations, using the sand and paper filters side by side, have been made on the same sample and the results obtained agreed to a thousandth. It was found best to wash the sand filters, used to catch the ammonium phosphomolybdate, with ammonia as well as with nitric acid, since in the ammonia washings silica and alumina were found, and these would tend to clog the reductor.

Once made up, they stand ready for repeated use, and besides saving time they save considerable money, especially where many determinations are made. By these filters, one man was able to turn out in one day forty-two phosphorus determinations, and every precipitate was washed until the droppings from the tube gave no reaction for molybdenum when tested with ammonium sulphide.

The cut shows clearly the man of making up these filters.

CHEMICAL LABORATORY, CARPENTER STEEL CO.,
READING, PA.

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[1] "Methods for the Analysis of Ores, Pig Iron, and Steel," compiled from the Transactions of the Chemical Section of the Engineers' Society of Western Pennsylvania.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF LAFAYETTE COLLEGE.]

SILICA AND INSOLUBLE RESIDUE IN PORTLAND CEMENT.

BY P. W. SHIMER.

Received February 14, 1899.

IT is desired, in this brief note, to call attention to a possible source of error in the determination of silica in cement, as usually carried out in many laboratories. In the method almost universally used the steps are as follows: Solution, with careful stirring, in either hydrochloric acid alone, or with addition of nitric acid; evaporation to dryness; solution, filtration, and ignition of the siliceous residue, without treatment with hydrofluoric acid. The insoluble residue is calculated as silica. The results are claimed to be accurate to within 0.20 per cent., and it is no doubt true, as claimed, that it is not possible to get duplicate samples of cement from the same bins, in which the average disagreement will be less than this. If the error in the silica determination were no greater than 0.20 per cent., it would not, practically, be important.

The writer has recently met with four samples of Portland cement in which the differences between the silica determined by solution in hydrochloric acid and by the fusion method were 2.48, 2.46, 1.10, and 1.00 per cent. If the silica determined by the acid method were treated with hydrofluoric acid, there is no doubt the results by that method would be sufficiently accurate.

In the case where there was a difference of 2.48 per cent. between the silicas by the two methods, we have complete analyses of the cement by each method of solution. The silica by the acid method was 2.48 per cent. high, while all the other determinations were correspondingly lower than the determinations by the fusion method. Alumina was 1.24 per cent. low; ferric oxide was 0.64 per cent. low; lime, 0.28 per cent.; magnesia, 0.12 per cent.; and sulphur trioxide was 0.14 per cent. low. The total of these differences is 2.42 per cent., thus showing conclusively to what the contamination of the silica by the acid method was due.

The discrepancies in the other three analyses are similarly accounted for. The excess of 2.46 per cent. in the silica by the acid method in the second sample, is balanced by a deficiency of 2.30 per cent. in the other determinations. The excess of 1.10 per cent. in the silica by the acid method in the third cement, is balanced by a deficiency of 0.96 per cent. in the other determination.

The excess of 1.00 per cent. in the silica by the acid method in the fourth cement, is balanced by a deficiency of 1.12 per cent. in the other determinations. It is interesting to note, in this connection, that the physical tests of the first two samples of cement, which showed differences of 2.48 and 2.46 per cent. between the two silicas, showed marked inferiority as compared with the two samples in which the differences between the silicas were 1.10 and 1.00 per cent.

This would point to insufficient clinkering or sintering of the first two cements. In other words, the burning of the cement was not at a high enough temperature, or was not continued long enough to completely decompose the insoluble silicates of alumina and to convert them into silicates and aluminates decomposable by hydrochloric acid. I have no doubt whatever, that when a Portland cement is properly compounded and correctly burned, the silicates and aluminates are easily decomposable by hydrochloric acid, and therefore the silica may be determined with very close approximation to the correct figures by the acid method. On standard cements, of good reputation, I have never found a greater difference than 0.20 per cent. between the silicas by the two methods. However, when the cement is not properly compounded and correctly burned, there will be a notable difference between the two silicas. The determination of silica by the two methods would thus appear to furnish an excellent means of getting valuable information as to the quality of the cement. When the two silicas agree, it means that all silicates and aluminates are decomposed by hydrochloric acid, and therefore are in an active hydraulic condition. When there is a large difference between the two silicas, it means the presence in the cement of unconverted and inert silica and alumina. In other words, the clay matter that the burning should have converted into active hydraulic combinations with lime, remains unconverted and inert.

In a sample of natural cement of low grade the silica by fusion was 26.90 per cent.; by the acid method it was 31.45 per cent., a difference in this case of 4.55 per cent., proving conclusively that, while the acid method may be very useful when used by an experienced chemist at a cement works making regularly a uniform product, it is not at all to be relied on as a universal method to be used indiscriminately for the determination of silica in all cements.

[CONTRIBUTIONS FROM THE UNITED STATES LABORATORY, BOSTON, MASS.]

ANALYTICAL RESEARCH ON SOD OIL.

BY ERASTUS HOPKINS, D. L. COBURN, AND EDW. SPILLER.

Received November 3, 1898.

EXCEPTING among the tanners very little is known of this oil, and among them it is known only in its principal application. Its chemical properties are little known and the aim of this paper is to state the main chemical facts regarding this oil, thousands of tons of which are used each year in the currying of leather.

To better understand what sod oil is, let us say that it is an oil which has for its basis various non-drying oils and greases, but almost exclusively cheap fish oils. These oils are put into the leather for currying purposes and the excess is extracted by various methods. The extracted oil has undergone a change from the original oil by coming in contact with the leather and becomes what is known in commerce as 'sod oil,' more highly valued by the tanners than the original oil.

In "Oils, Fats and Waxes," Benedikt and Lewkowitsch describe this oil as follows: "Sod oil or dégras is the waste fat obtained in the chamoising process and is used for currying purposes; *i. e.*, dressing bark-tanned leather." Dégras proper might be said to be the oil obtained from skins in the manufacture of chamois leather, while its allied substance, sod oil, is the oil obtained from ordinary leather.

The principal oils used from which to make sod oil are menhaden and cod oils, but various oils (even olive oil) and greases may be used, and hence give to the sod oil a variation in constants which have so extended a range that they might not be constants at all.

Sod oil has the odor of leather and is generally of such a character that it forms a separating emulsion. The color may be a light yellow to a dark brown. Its viscosity may vary from that of a pure oil to a thin grease with a specific gravity of from 0.96 to 0.99.

The noticeable chemical characteristics are the presence of a so-called 'dégras former' hide fragments, and a high ash content due to the leather from which the oil is extracted. Another point of interest is the great variation in moisture and mineral acid of the oil, as well, of course, as of all its constants.

It is claimed that the higher the percentage of 'dégras former' and the lower the percentage of mineral acid, the more valuable the oil, but commercially the price of the oil does not seem to be governed by these facts, but is bought and sold on firm names, which is undoubtedly due to the fact that tanners still work by the "thumb rule" rather than by being advised by scientific research.

We hope in this paper to bring out the general analytical facts regarding the oil itself and later to work up the almost unknown dégras former which is described as a resinous substance (not a resin) found in sod oil, melting at 65°–67°, and showing certain degrees of solubility with various solvents. Dégras former, as it occurs in sod oil, can be extracted from sod oil by petroleum ether, but in its pure state dégras former is insoluble in this menstruum.

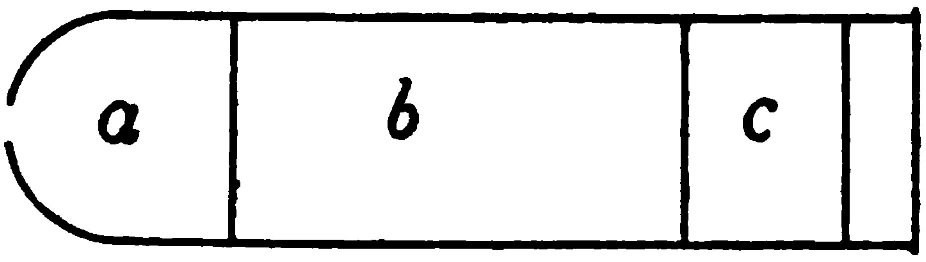
Sod oil contains unsaponifiable and saponifiable oil, the unsaponifiable being undoubtedly due to the unsaponifiable matter in the fish oil used. It contains also moisture, soap and hide fragments, ash and dégras former, and we have endeavored to find a rapid process by which moisture, oil, soap, and hide fragments could be determined which will be described below under that subject. The samples of sod oil taken were commercial and imported sod oils.

MOISTURE, OIL, SOAP, AND HIDE FRAGMENTS.

After some preliminary work on the determination of moisture, oil, soap, and hide fragments, it was found that the methods described by Benedikt and Lewkowitsch were rather tedious, and the results in our hands were unsatisfactory. This was particularly true of the moisture which we attempted to determine by weighing the oil with pure ignited sand (enough to absorb it), and by drying at 120° C. in a drying oven. We were unable to get a constant weight by this method, the oil continuing to lose weight even after five or six days drying.

The following method was then devised and found to give accurate results:

For the analyses we used a test-tube of sixty to eighty mm. in length and fifteen to twenty mm. in diameter with a small hole blown in its bottom, and furnished with a platinum wire for suspending the tube while weighing. A small wad of absorbent cotton is first inserted into the tube (*a*), then an ashless filter paper of twelve cm. diameter is folded about the finger (placing the tip of the finger in the center of the paper) and placed in the test-tube so that upon withdrawing the finger from the inside of the filter-paper, the paper with its closed end on the cotton wad takes the shape of the test-tube and forms a filter-paper capsule which prevents the solid matter of the oil from being mechanically carried through the cotton. The capsule is made of filter-paper because it was found that the ordinary capsule is too large and heavy for this work. The inside of this filter-paper capsule is filled with closely rolled ashless filter-papers (*b*) and a cotton wad is put on top (*c*). This is dried and weighed for tare. The upper wad is then removed and the sod oil introduced and absorbed by the filter-paper, care being taken that the oil does not saturate the lower cotton wad. The upper wad is then replaced and the weight taken gives the charge of oil. The test-tube after weighing is placed in a water-jacket drying-oven and attached by the lower end of the tube to a suction-pipe which, under slight pressure, draws hot air through the test-tube from the top, out through the hole in the bottom. By using a water-jacket oven the temperature is ensured to remain constant at 100° C. and the suction of hot air makes the drying to constant weight rapid when compared to other methods used for the



drying of oils. The loss in weight gives the moisture. The tube containing the anhydrous oil is placed in a Soxhlet apparatus, and the oil is extracted by 40° petroleum-ether. A weight taken on the dried tube, or better on the extracted oil, gives the oil, etc., soluble in petroleum-ether. There are now left in the tube soap, hide fragments, and ash. The test-tube is next treated in the Soxhlet with alcohol which extracts the soap. A weight on the tube gives (1) by loss, soap, etc., soluble in alcohol, (2) hide fragments and ash insoluble in petroleum-ether and alcohol, and upon igniting the cotton and filter-paper this ash is determined and the difference gives the amount of hide fragments.

The ash found is lower than total ash, and this difference is accounted for by finding fractions of the ash in the oil and soap. For absolutely accurate analytical work the ash soluble in petroleum-ether and alcohol should be determined and subtracted from the oil and soap and added to the ash of ignition, but the error is so small that for commercial work this can be omitted as we have omitted it in this research. Upon making determinations of these ash fractions we have found that their sum checks the total ash. All of these determinations are made upon one charge which is an advantage in itself.

The process is rapid and gives very accurate results, and its use is not in any way confined to sod oil, but may be used in the analysis of all oils and greases where drying and extraction are required. Because of the necessarily small test-tube used we found that a Soxhlet apparatus with a two-inch siphon tube instead of the regulation four-inch tube was better adapted to the work.

TOTAL ASH.

This is determined by igniting the oil in a tared platinum dish. The ash is found to be high, and consists chiefly of calcium, iron, and the alkalies for bases with carbon dioxide and sulphur trioxide for the acid radical. The calcium comes from the lime used in liming hides.

DÉGRAS FORMER.

For this determination Jean's method, mentioned by Benedikt and Lewkowitsch, was followed except in certain modifications, which we found to be necessary because of the lack of concordant results. His method advises decantation of the liquid from the crust of dégras former: this we found inaccurate because by decantation small particles of dégras former were carried away, and for this reason we used a filter and transferred the crust of dégras former upon the filter. Another point which he omits to state is that oil often adheres to the dégras former and thus causes too high results; this we obviated by washing the dégras former with petroleum-ether after having washed it free of acid and salt. Jean dissolves the dégras former in ether but we found that it took too long and too much solvent, whereas it is readily soluble in absolute alcohol and gives a pure product melting at the required temperature.

Our modified Jean's method is as follows: The oil is saponified according to the method for the determination of unsaponifiable matter. (The unsaponifiable number may thus be determined on the same charge.) The saponifiable matter of the sod oil which contains the easily saponifiable dégras former, is heated to drive off the alcohol and ether used in the saponification. The saponifiable matter is taken up with water, and the soap is precipitated hot with an excess of salt. The mixture is cooled and filtered off into a beaker and hydrochloric acid is added to the filtrate. The dégras former is precipitated by hydrochloric acid in flocks which unite on boiling and adhere to the sides of the beaker on cooling, leaving a soft brown crust on the top of the solution. The liquid is filtered off (filtering being used rather than decantation to prevent loss); the dégras former is washed with water free from acid and salt and then with petroleum-ether free from oil. It is then dissolved on the filter with absolute alcohol; the alcohol is driven off and the dégras former weighed. This dégras former should melt at 65°–67° C.

GENERAL ANALYTICAL TESTS.

The analytical tests, common to oil analysis, and made by us with only a few modifications, were the determinations of total KOH, mineral acid, total acid, from which were calculated the KOH number, ether number, and free fatty acid number, also of Reichert-Meissl, iodine value, unsaponifiable, and iodine of unsaponifiable. All of these were calculated to anhydrous sod oil and also to numbers "In terms of oil, etc., soluble in petroleum-ether." The methods are so generally well known that they are not given excepting where modifications of the same were found advisable.

The total KOH was determined upon two and one-half grams of the oil and the final titration was made with half-normal hydrochloric acid with phenolphthalein as indicator. It is rather difficult to determine the end-point in these oils because of the high color of the oil, but if, when the end-point is near, the flask is vigorously shaken a foam will appear on the surface of the liquid. If a drop of phenolphthalein is now added, the foam will become pink until the neutral point is reached. The calculation is to milligrams of potassium hydroxide per one gram of sod oil.

The mineral acid was determined by boiling in distilled water two to two and one-half grams of the sod oil and washing on a filter with hot distilled water until all the mineral acid was removed. This is titrated with standard sodium hydroxide and calculated to milligrams of potassium hydroxide per one gram of sod oil.

The total acid was determined by dissolving two grams of oil in hot methyl alcohol in which all the free acid has been neutralized. This alcoholic solution is titrated with standard sodium hydroxide and calculated to milligrams of potassium hydroxide per one gram of sod oil.

The KOH number is calculated as the difference between the total KOH and mineral acid.

The ether number is calculated as the difference between total KOH and total acid.

The free fatty acid is calculated as the difference between the total acid and mineral acid.

The Reichert-Meissl value, iodine number and unsaponifiable number were determined by the common methods with no modifications.

The petroleum-ether used throughout these experiments and analyses was 40° naphtha which as a separating medium was found to be essential, and as a solvent acted more rapidly and with better results than the lower fractions of naphtha.

The numbers obtained by the above methods differ very

								Dégras former.			1. Total KOH.		
Sod oil.	Total ash.	Moisture.	Oil, etc., soluble in petroleum-ether.	Soap, etc., soluble in alcohol.	Hide fragments.	Ash insoluble in petroleum-ether and alcohol.	Total.		Anhydrous.	In terms of oil, etc., soluble in petroleum-ether.		Anhydrous.	In terms of oil, etc., soluble in petroleum-ether.
1. Yellow	0.96	25.27	72.60	1.90	0.66	0.12	100.55	0.93	1.24	1.28	99.07	132.57	136.46
2. Brown	0.70	3.38	88.61	7.05	1.05	0.15	100.24	15.98	16.54	16.91	206.51	213.73	233.05
3. Brown	0.215	2.75	96.60	1.32	1.09	0.16	101.92	2.73	2.81	2.83	111.52	114.67	115.44
4. Yellow	0.05	19.48	....	....	....	....	....	....	....	....	108.75	135.06	......
5. Brown	1.045	15.45	75.37	7.24	1.26	0.47	99.79	6.33	7.48	8.39	140.59	166.26	186.53
6. Yellow	0.68	30.87	59.74	8.81	0.49	0.06	99.97	2.65	3.84	4.43	85.70	123.97	143.46
7. Brown	0.37	4.59	89.59	3.09	2.99	0.15	100.41	21.41	22.44	23.89	181.53	190.05	202.40
8. Brown	0.77	33.46	58.81	5.40	2.24	0.35	100.26	17.73	26.64	30.14	135.83	204.13	230.96
9. Brown	0.55	1.01	95.69	2.44	0.79	0.13	100.06	13.91	14.05	14.53	186.53	188.43	194.93
10. Brown, thick.	0.36	40.61	56.62	3.19	0.31	0.22	100.95	0.65	1.09	1.15	64.04	107.83	113.10
11. Brown, thin ..	0.28	3.94	94.38	2.57	0.15	0.16	101.20	2.74	2.85	2.90	101.48	105.64	107.32
12. Brown	0.46	23.70	73.36	0.68	1.29	0.15	99.18	8.41	11.02	11.46	109.94	144.09	149.86

Sod oil.	2. Mineral acid.			3. KOH number. 1 — 2 = 3.			4. Total acid.			5. Ether number. 1 — 2 = 3.		
		Anhydrous.	In terms of oil, etc., soluble in petroleum-ether.		Anhydrous.	In te.ms of oil, etc., soluble in petroleum-ether.		Anhydrous.	In terms of oil, etc., soluble in petroleum-ether.		Anhydrous.	In terms of oil, etc., soluble in petroleum-ether.
1. Yellow	20.77	27.79	28.62	78.30	104.78	107.84	48.20	64.50	66.39	50.87	68.07	70.07
2. Brown	3.16	3.28	3.56	203.35	210.45	229.49	75.80	78.48	85.54	130.70	135.28	147.51
3. Brown	1.63	1.67	1.68	109.89	113.00	113.76	46.32	47.63	47.95	65.20	67.04	67.49
4. Yellow	1.07	1.33	....	107.68	133.75	....	27.20	33.78	....	81.55	101.28	....
5. Brown	0.96	1.13	1.27	139.63	165.13	185.26	74.14	87.69	98.37	66.45	78.57	88.16
6. Yellow	24.07	34.82	40.29	61.63	89.15	103.17	57.06	82.54	95.51	28.64	41.43	47.95
7. Brown	64.77	67.88	72.29	116.56	122.17	130.11	84.17	88.22	93.95	97.16	101.83	108.45
8. Brown	52.54	77.96	89.34	83.29	126.17	141.62	70.50	105.95	119.88	65.33	98.18	111.08
9. Brown	90.50	91.51	94.57	96.03	96.92	100.36	124.50	125.77	130.11	62.03	62.66	64.8$_2$
10. Brown, thick .	7.70	12.96	13.60	56.34	94.87	99.50	55.21	92.96	97.51	6.83	14.87	15.59
11. Brown, thin ..	22.20	23.11	23.52	79.28	82.53	84.00	61.83	64.37	65.51	39.65	41.27	41.81
12. Brown	10.58	13.86	14.42	99.36	130.23	135.44	30.90	40.49	42.12	79.04	103.60	107.74

Sod oil.	6. Free fatty acid. 1 — 4 = 5			Reichert-Meissl number.			Iodine number.			Unsaponifiable number.			Iodine of unsaponifiable.
		Anhydrous.	In terms of oil, etc., soluble in petroleum-ether.		Anhydrous.	In terms of oil, etc., soluble in petroleum-ether.		Anhydrous.	In terms of oil, etc., soluble in petroleum-ether.		Anhydrous.	In terms of oil, etc., soluble in petroleum-ether.	
1. Yellow	27.43	36.71	37.77	1.87	2.50	2.58	52.45	70.18	73.76	20.60	27.56	28.39	31.76
2. Brown	72.64	75.17	81.98	2.66	2.75	3.00	60.54	62.66	68.32	0.95	0.97	1.07	9.38
3. Brown	44.69	45.96	46.27	2.53	2.60	2.69	43.56	44.79	45.01	41.46	42.62	42.92	16.89
4. Yellow	26.13	32.45	....	2.24	2.66	....	55.02	68.33	....	18.95	23.53	....	22.48
5. Brown	73.18	86.56	97.10	2.41	2.85	3.19	46.69	55.22	61.94	14.90	17.62	19.77	20.80
6. Yellow	32.99	47.72	55.22	1.35	1.95	2.26	49.03	70.92	82.07	14.99	21.68	25.09	23.66
7. Brown	19.40	20.34	21.66	1.66	1.74	1.85	59.06	61.90	65.92	0.58	0.61	0.64	3.22
8. Brown	17.96	27.99	30.54	3.72	5.59	6.32	44.17	66.38	75.11	2.80	4.21	4.76	52.07
9. Brown	34.00	34.26	35.54	2.58	2.61	2.69	77.53	78.32	81.02	0.37	0.37	0.38	71.58
10. Brown, thick	47.51	80.00	83.90	2.02	3.41	3.56	22.79	38.37	40.25	21.81	36.72	38.52	13.80
11. Brown, thin	39.63	41.26	60.48	2.33	2.43	2.47	47.19	49.12	50.00	29.85	31.07	31.63	25.19
12. Brown	20.32	26.63	27.70	3.87	5.07	5.27	41.01	53.74	55.90	6.32	8.28	8.61	20.95

widely, as can be seen by the accompanying tables, and this is true whether the numbers are referred to the anhydrous sod oil or to the "oil, etc., soluble in petroleum ether." Calculations were also made in terms of "oil, etc., soluble in petroleum-ether less dégras former," but as no concordant results were obtained we did not think it necessary to add another column of figures.

The reason for this variation in figures seems to be the great variety of oils which are used for the making of sod oil as well as the different modifications of treating the same initial oil by different makers. Still, sod oil, by a complete analysis as described above, can be easily distinguished from other oils.

CORRESPONDENCE RELATING TO THE BERZELIUS MEMORIAL SERVICES.

Held in Stockholm, Sweden, October 7, 1898, on the occasion of the fiftieth anniversary of the death of Berzelius.

" *The American Chemical Society :*

Messieurs, chers et honorés collègues: À l'occasion du cinquantieme anniversaire de la mort de Berzelius, l'Académie des Sciences de Stockholm, la Faculté de Médicine de Stockholm (Karolinska Institutet), l'Académie d'Agriculture et la Société des Médecins de Suède se proposent de célébrer la memoire du grand savant par une fête commémorative.

Au nom de ces institutions nous avons l'honneur de vous prier de bien vouloir déléguer un de vos membres pour prendre part à cette solennité, qui aura lieu à Stockholm le 7 octobre 1898.

Veuillez, messieurs et chers collègues, agréer l'assurance de nos sentiments les plus distingués.

A. E. NORDENSKIOLD,
L. F. NILSON,
F. LENNMALM,
CHRISTIAN ZOVEN,
SEVERIN JOLIN.

"551 PUTNAM AVE., BROOKLYN, N. Y.,
September 30, 1898.

DR. A. E. NORDENSKIOLD, Academy of Sciences, Stockholm, Sweden.

Dear Sir: I have the honor to acknowledge the receipt of the communication sent by yourself and colleagues announcing the solemnities in commemoration of Berzelius, on the occasion of the fiftieth anniversary of his death, to be held in Stockholm, October 7, 1898, under the auspices of the Academy of Sciences of Stockholm, the Faculty of Medicine of Stockholm (Karolinska Institutet), the Academy of Agriculture, and the Medical Society of Sweden.

Permit me also to acknowledge with thanks the request that the American Chemical Society send one of its members as a delegate to take part in this memorial occasion, and to express regret that at the present time none of our members are available as active delegates from the United States. I take pleasure in informing you, however, that honorary delegates have been chosen to represent the American Chemical Society, and to prepare a suitable memorial.

The chemists of America would vie with those of the old world in paying their tribute of reverence to the name and fame of Berzelius, and in recognizing his distinguished services to chemistry and kindred sciences. While no one from this country may be able to participate actively in the solemnities, we would nevertheless not allow the occasion to pass without expressing our great interest in it, and the profound feelings which it awakens among the chemists on this side the Atlantic.

The following named are the members appointed as honorary delegates to represent the American Chemical Society:

WOLCOTT GIBBS, *Chairman*,[1]
GEORGE F. BARKER,
WILLIAM McMURTRIE,
HARVEY W. WILEY,
ALBERT B. PRESCOTT,
F. W. CLARKE,
J. W. MALLET.

Very respectfully yours,

ALBERT C. HALE,
Secretary of the American Chemical Society."

The following cablegram was sent in time to be received at the meeting:

October 6, 1898.

"TO A. E. NORDENSKIOLD, Academy of Sciences, Stockholm, Sweden.

The American Chemical Society reveres the memory of Berzelius who conferred luster on our science.

CHARLES E. MUNROE, *President.*
ALBERT C. HALE, *Secretary.*"

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[1] The Committee is given here as finally constituted.

NOTE.

A Method for Cleansing Burettes.—Globules of liquids may adhere to the inner walls of burettes, when they are emptied. The tendency can be removed by allowing a weak solution of chromic acid to stand in the burette for a few hours.

The solution may be made by adding ten grams of potassium bichromate to fifty cc. water and five cc. concentrated sulphuric acid. Pour it in the burette and allow it to remain over night. The solution does not injure the rubber tube of a Mohr burette. Wash the burette well with water. WILLIAM GLENN.

NEW BOOKS.

CHEMISCHE TECHNOLOGIE AN DER UNIVERSITÄTEN UND TECHNISCHEN HOCHSCHULEN DEUTSCHLANDS. By DR. FERDINAND FISCHER, University of Göttingen. Braunschweig: Friedrich Vieweg und Sohn. pp. 54. Price, M. 1.25.

In 1897 Dr. Fischer published "Das Studium der technischen Chemie an der Universitäten und technischen Hochschulen Deutschlands, und das Chemiker-Examen," in which he set forth the status of the subject at that time. The present pamphlet is intended merely as a supplement to that work. It consists of abstracts of addresses, papers, and published articles by leading authorities of Germany, with comments by the author (Fischer) upon some of the articles.

Chemical technology was first included in a university course at Göttingen in 1766 and within a few decades nearly all the universities included it as a major course. For many years at Giessen, Liebig lectured on the subject; an interesting program of the chemical course there, for the years 1809 to 1852 inclusive, is given. With the establishment of the Technische Hochschule, technical chemistry gradually disappeared as a major course in the universities, the last full professor in this subject being Prof. Wagner of Würzburg, who died in 1880. At the present time, in nearly one-half of the German universities, the subject is not taught, but a movement is now on foot to reestablish it and one of the objects of this book is to further the movement.

The state examination of technical chemists is also discussed and apparently much difference of opinion exists among the leading chemists as to its desirability. But nothing seems to have come of the agitation in its favor, and further action on the question is indefinitely postponed. The book closes with a statement of the purposes of the "Association of Laboratory Directors, etc.," and the regulations adopted to govern examinations for diploma and doctor's degree. F. H. THORP.

LABORATORY WORK IN PHYSIOLOGICAL CHEMISTRY. BY FREDERICK G. NOVY, Sc.D., M.D., Junior Professor of Hygiene and Physiological Chemistry, University of Michigan. Second Edition, Revised and Enlarged. Ann Arbor: George Wahr. 1898. pp. 326. Price, $2.00.

The second edition of this work is wholly rewritten, and is practically a new book. It contains directions for laboratory work covering the various food-stuffs and the fluids and secretions of the body, together with brief explanatory descriptions of these substances, and is designed to guide the student in the experimental study of chemistry in its broad relations to physiology, hygiene, and disease. In the latter part of the work, about sixty pages are devoted to quantitative analysis. The experiments and subject-matter are well selected and concisely described without omitting important details. The course may be covered by a class devoting a half-day, daily, for three months to the work. The book will be found useful both in undergraduate college courses and in the medical school where a well-equipped laboratory is at the command of students and teacher.

A noticeable defect in the application to clinical use of the methods taught is the omission of definite information regarding physiological variations. Thus, on page 295, we read, "There is an excess of phosphates in the urine in inflammatory diseases of the nervous system and in rickets and osteomalacia. There is deficiency in indigestion and in structural diseases of the kidney;" and again, "A quantitative analysis will show the presence of an excess or deficiency of phosphates." In describing phosphoric acid in urine, the text states "On an average 2.5 g of P_2O_5 are excreted per day." What variation, then, from this amount is to be considered an excess or deficiency? The author does not state. If the determination is to serve any practical purpose, evidently some more definite method of interpretation of the result obtained must be available. This is likewise true of the amounts of the constituents of the gastric juice, breast milk, etc., as well as of urine. Information along these lines is looked for and best taught with the technical methods to be employed.

Prof. Novy's work marks a distinct advance in a field, the future of which is as promising as that of any department of experimental physiology and medicine. His work is a foremost laboratory guide in a subject demanding a place in the curriculum of every medical school which undertakes to instruct its students in the technic of modern scientific medicine.

E. E. SMITH.

ELECTROLYSIS AND ELECTROSYNTHESIS OF ORGANIC COMPOUNDS. BY DR. WALTHER LÖB, Privatdocent in the University of Bonn. Translated by H. W. F. LORENZ, A.M., Ph.D., Graduate of the University of Berlin. New York: John Wiley and Sons. Price, $1.00.

This unpretentious little volume gives, in the space of about 100 pages, what may be fairly termed the substance of all that has been accomplished by the electric current in the domain of organic chemistry. The most recent views in regard to reductions and oxidations are given in sufficient detail to satisfy the inquiring student. The first half of the book considers the aliphatic compounds, the second half the aromatic derivatives. It must be remarked, however, that the completeness of such works as those of Tommasi and of Peters is not found here, although the essentials and the latest results are everywhere present. It is a most suggestive compilation and the student, eager to take up problems in this comparatively new field of research, will find hints upon almost every page as to lines of investigation, which would amply repay his experimental inquiries. Not as a criticism, but simply to arrest an erroneous notion the reviewer would call attention to a statement made on page 18, relating to the electrolysis of metallic acetates. It is there said of uranium acetate that from its solution the current separates the metal, which passes to the anode. This is wrong. Metallic uranium cannot be obtained in this way. It is the hydrate which is deposited at the cathode. Again, on page 25 occurs the sentence "on this property depends the great importance of oxalic acid in quantitative electrolytic analysis, into which it has been introduced by Classen." Would it not be just as well to credit Parodi and Mascazzini with having first applied oxalic acid in this way? They first used this acid in the electrodeposition of iron, after which Classen extended its use by the elaboration of methods for the electrolytic determination of other metals. The closing paragraph of the book calls attention to the "important points which promise to be of great assistance ... in connection with future research in the field of organic chemistry; ... the oxidation reactions which occur in the electrolysis of acids of the aliphatic series, the reduction reactions in the case of the aromatic series, and lastly the reactions involving substitutions. ... Of these the first is apparently the most promising." The translator has performed his task with great credit to himself.

The reviewer has read the book with pleasure and profit, and is confident that it will be regarded as a welcome addition to our rapidly increasing electrolytic literature.

EDGAR F. SMITH.

MICHAEL FARADAY, HIS LIFE AND WORK. BY SILVANUS P. THOMPSON. New York: The Macmillan Co. 1898. xii + 308 pp. 12mo. Price, $1.25.

The "Century Science Series", of which this volume forms a part, has already issued biographies of Pasteur, Davy, Dalton, and Liebig, as well as of men of science distinguished in other departments than chemistry; but no one of those known to the writer is so charmingly written as that under review. Professor Thompson, it is true, had an uncommon man to portray, simple in his nature and grand in his achievements, and the biographer has most successfully depicted both characteristics. Michael Faraday's life is attractively described by one who sympathizes thoroughly with the gentle, lovable man, and at the same time his scientific work is skilfully reviewed by one well qualified by his own attainments to understand and appreciate it.

In his preface Dr. Thompson refers to the previous biographies of Faraday by Bence Jones, Tyndall and Gladstone, each having special merits, and modestly says "there seems room for another account of the life and labours of the man whose influence upon the century in which he lived was so great", and this volume justifies the remark.

If there be such a thing as the "spontaneous generation" of genius surely Faraday affords a striking example; the son of a working blacksmith and a farmer's daughter, born in humble circumstances in a village near London, receiving very little schooling, serving seven years of apprenticeship to a bookbinder, reaching the age of twenty before he had an opportunity of attending a single lecture on natural philosophy, these conditions would hardly be deemed favorable for producing an intellectual genius, a master in science, whom all peoples on earth delight to honor. That Faraday attained such eminence is plainly due to two controlling factors in his moral nature, an intense love for the truths of nature and indefatigable perseverance, both of which were applied to overcoming obstacles that had baffled many. Faraday's first menial position with the rather haughty Davy, their travels on the continent, which afforded Davy's "valet" so much distress as to partly counterbalance the advantages; Faraday's early studies at the Royal Institution, becoming so noteworthy as to arouse some jealousy in Davy, who, however, soon learned to appreciate the rising philosopher; the simple life of the assistant with his bride in two rooms at the top of the Royal Institution, on £100 a year; his admission into the Royal Society; all these interesting details are narrated in the first two chapters. Then follows an account of the masterly researches in electricity and magnetism, which for convenience is divided into three periods; two chapters are devoted to the circumstances of his later life and to his views on the pursuit of science and on education, and a final chapter deals sympathetically with the religious views of the simple-minded Sandemanian.

Through the pages of the volume are interspersed letters written by Faraday to his intimate friends, facsimiles of the rude sketches of novel apparatus drawn in his note-books, and a few woodcuts of scenes and objects associated with him.

Dr. Thompson remarks that he never ceases to regret that he never met Faraday, but no one of those who did know him has so well portrayed him. A charming portrait of Faraday etched by Dr. Thompson forms the frontispiece to a biography that ought to be studied by every one interested in the development of the physical sciences. HENRY CARRINGTON BOLTON.

TEXT-BOOK OF MEDICAL AND PHARMACEUTICAL CHEMISTRY. BY ELIAS H. BARTLEY, B.S., M.D., Ph.G. Fifth Edition, Revised and Enlarged. Philadelphia: P. Blakiston's Son and Co. 1898. 738 pp. Price $3.00.

The demand for a fifth edition of a work is a most substantial tribute to its merit. A quality that has largely contributed to create such a demand, in this instance, is that the subject-matter of Prof. Bartley's work is especially adapted to meet the requirements of those for whom the book is designed. It is not too voluminous for the medical and pharmaceutical student nor too foreign to his interests.

In Part 1 (about 70 pages) the author presents the fundamental facts of chemical physics. Part 2 (about 40 pages) is devoted to theoretical chemistry, followed in Part 3 (nearly 200 pages) by descriptive inorganic chemistry. The author adopts Mendelejeff's classification of the elements, at the same time retaining the distinction of metals and non-metals. Part 4 (234 pages) is occupied with descriptive organic chemistry, including vegetable and animal proximate principles. The last section of the text, Part 5 (137 pages), is devoted to physiological and clinical chemistry. The author's familiarity with the subject and good judgment in the selection of material are well illustrated in the chapter on foods and diets which contains in less than thirty pages an unusually comprehensive and yet simple presentation of the chemistry of these subjects.

It is to be regretted that the author does not insist upon numerical urinary standards. An attempt to judge of the amounts of various constituents of urine by observing the bulks formed when they are precipitated is of little real value. Such methods are not chemical analysis and have no place in a chemical text-book. Moreover, they rob the clinician of what service a real knowledge might render.

The historical lists of tests for albumin and sugar in urine, which the text records, could with advantage be replaced by descriptions of selected methods. It is the more desirable, in this instance, since these tests are so important and yet confusing to those unaccustomed to urine analysis.

An appendix of twenty pages containing various tables increases the value of the book for reference, while a glossary and complete index render its subject-matter readily available. It is not speaking too highly of Prof. Bartley's work to say that it takes first rank among text-boks on medical and pharmaceutical chemistry.

E. E. SMITH.

ESSENTIALS OF MATERIA MEDICA, THERAPEUTICS, AND PRESCRIPTION WRITING. Saunders' Question-Compends, No. 7. BY HENRY MORRIS, M.D. Fifth Edition. 288 pages. Philadelphia: W. B. Saunders. Price $1.00.

This little book belongs to a class which has become very popular with students of medicine in the last ten years, and, like the others, it is arranged in the form of questions and answers. As a matter of necessity the information it presents is very greatly condensed, furnishing often not more than an outline of the subject. It is, therefore, in extent, just about what the student needs and uses when "cramming" for an examination. It is possible that books of this class may be legitimately used, and thus possess for the student a real value, but in general their use is to be regretted as tending to encourage superficial reading. The present book seems to be, in the main, carefully compiled, and as free from error as can be expected with such condensation. A careless statement, or mistake, is found at the bottom of page 203, however, where it is said that potassium salts convert uric acid into the more soluble urea. The accuracy of the statement on page 206, regarding the solubility of lithium urate, is also questionable. J. H. LONG.

A MANUAL OF CHEMICAL ANALYSIS; QUALITATIVE AND QUANTITATIVE. BY G. S. NEWTH, F.I.C., F.C.S., Demonstrator in the Royal College of Science. London: Assistant Examiner in Chemistry, Science and Art Department. New York, London, and Bombay: Longmans, Green and Co. 1898. xii + 462 pp. Price, $1.75.

To all who value the previous works by Newth, " Chemical Lecture Experiments," and his two text-books on " Inorganic Chemistry," the appearance of the present manual on analysis will certainly be most welcome. As might naturally be expected from its predecessors, the manual is replete with modern methods of manipulation, clever devices to simplify time-honored reactions, and clear, concise explanations. The fundamental processes of quantitative analysis are accompanied by a wealth of illustration, which should enable the dullest intellect to grasp the successive steps in weighing, filtering, the incineration of filters, the ignition of crucibles, etc. These features could be confidently counted upon in advance.

The plan of the work is of course open to criticism. The qualitative part, which includes a fairly generous treatment of the rarer elements, and less common acids, occupies 188 pages; gravimetric and volumetric quantitative analysis extend also over 188 pages; gas analysis covers 37 pages, ultimate organic analysis, 20 pages; and physico-chemical determinations 10 pages. Whether it is desirable to place a manual of this size in the hands of the beginner in qualitative analysis will be a moot question, in the future, as in the past. Dr. Caldwell has solved the question to some extent in his manual of analysis, limiting the qualitative work to the more common bases and acids, and the quantitative feature to ten or fifteen of the more typical determinations. Frequent editions show that the book has met a distinct need. Dr. Muter and Dr. Long have each published successful manuals on a somewhat more extended scale, providing for medical and pharmaceutical students all necessary qualitative and quantitative instruction in a single volume. The writer doubts the expediency of placing a manual of the nature of Professor Newth's, in the hands of those who have no intention of advancing beyond a course in qualitative analysis. The abundance of detail, and the fact that over one-half of the contents of the book will never be put to practical use, seriously handicap its value for the ordinary college student. On the contrary, he regards it as admirably adapted for the present and prospective needs of such students as take up qualitative analysis as preliminary to more advanced laboratory work in chemistry. For such, the combination in one volume of directions and data covering the whole field of analysis is attended with manifest disciplinary and practical advantages. He has, in fact, not delayed to adopt at once, the manual under consideration, for the use of this category of students in his laboratory.

The arrangement of material is, as a rule, logical and satisfactory. In the qualitative part the important tests for each member of a group of bases, are first given and then the systematic treatment of the group follows, accompanied by a clear scheme. While detail is well worked out, it would seem as if the provision for a more compact and comprehensive survey of the entire field could be improved. Thus on page 16 is the general division of bases into groups; on page 17 is a table of the precipitates given by each group reagent. Group schemes are scattered through the following 160 pages. Then comes, *at the end*, "preliminary tests and operations," forming Chapter XVI. This chapter could advantageously contain a complete schematic summary of all tables given before for the detection of both bases and acids. Such an arrangement, similar to that which gives such value to the "Tabellen" of Will or Wallach in German, would vastly facilitate the use of Newth's manual for young and unformed minds.

The author has omitted argon and helium from the list of elements, with their atomic weights, and probably wisely, in view of the astonishing group of elementary gases isolated from argon during the past few months. The use of didymium in the same list, and the absence of neodymium, and praseodymium is a bit of conservatism hardly in keeping with the progressive nature of the book.

The number of novel and ingenious devices for carrying out qualitative tests, such as that on page 84 for securing the $CuCl_2$ flame, will render the book most helpful and attractive to young minds. Newth's declination on page 157, to describe odors, is eminently wise and recalls the great amusement which greeted a foreign chemist's recent account of a substance which possessed a "blumenartigen Geruch."

It is to be hoped that our American chemists will follow Newth's example, in adopting the system of standard reagents, devised by Reddrop.[1] In this system all laboratory reagents carry signatures indicating whether they are normal, or multiples or fractions of normal solutions. Thus about one-half of our ordinary reagents are strictly normal, $= N$; calcium sulphate is $\frac{N}{80}$; sodium hydroxide is 5 N, etc. In this connection Professor Newth could well designate a saturated solution of $Ca(HO)_2$, as $\frac{N}{20}$, and not prefix the qualification "about."[2]

While the manual has so many pronounced features of exceptional excellence it is not free from certain flaws and errors inevitable in a first edition. Thus in the list of reagents just referred to, we miss H_2PtCl_6, $K_2Cr_2O_7$, $NaHC_4H_4O_6$, etc. although directions for their use are given in several places.

Provision is made in this list for a normal solution only of ammonium sulphate, while on page 35, the directions call for a *strong* solution. Among faulty expressions, scarcely admissible in a college text-book, are "*nearly* soluble in alcohol," p. 23; "it is therefore *only* possible to have an aqueous solution of the ortho-acid," note p. 93; "bring the liquid once more *to the boil*,"

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[1] *Chemical News*, May, 1890.

[2] Cf. Golding: *J. Soc. Chem. Ind.*, 17, 125.

p. 48. The statements on p. 166 with regard to silicic acid, assigning H_2SiO_3 as the formula of the gelatinous precipitate and H_4SiO_4, as the formula of the soluble acid only, are not in harmony with the results of recent investigations in the writer's laboratory.[1] Both tartaric acid and hydrogen sodium tartrate, are used in testing for ammonium salts (p. 21), but the second reagent only is advised for potassium compounds.

The following omissions of analytical data should be remedied in a second edition; on p. 88, the frequent presence of sulphur in the residue of HgS, $PbSO_4$ and $Hg(NO_3)_2.2HgS$, is overlooked; on p. 70, a method for the separation of glucinum, zirconium, titanium, and uranium should be outlined; on p. 128, no mention is made of Hart's excellent method for mixtures of chlorides, bromides, and iodides; on p. 151, no mention is made of the combustibility of all hypophosphites—their most striking property; on p. 155, no mention is made of the reaction of formates with ferric chloride, nor of the prompt reaction with silver nitrate; on p. 169, the familiar test for silica, etc. by means of calcium fluoride and sulphuric acid is omitted; on p. 151, the deportment of metaphosphates with ammonium molybdate is not stated; on p. 171, pyrophosphoric, metaphosphoric, phosphorous and hypophosphorous acids are omitted from the general scheme for the systematic detection of acids, although such a rare acid as HCNO is included.

Despite these minor blemishes, the book marks a distinct advance in the evolution of the ideal manual of analysis, and will certainly find many friends. THOMAS H. NORTON.

AN INTRODUCTORY COURSE OF QUANTITATIVE CHEMICAL ANALYSIS WITH EXPLANATORY NOTES AND STOICHIOMETRICAL PROBLEMS. BY HENRY P. TALBOT, Ph.D., Professor of Analytical Chemistry in the Massachusetts Institute of Technology. Third Edition, Revised and Enlarged. 153 pp. New York: The Macmillan Co. 1899. Price $1.50.

That a third edition should be demanded in less than two years from the first appearance of this book, is evidence that many teachers have found it suited to their needs. To all the matter contained in the first edition, the present adds the determination of carbon dioxide in dolomite, the determination of silica in laumontite and in feldspar, reference to the determination of zinc

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[1] This Journal, 19, 832.

as the pyrophosphate, and a very clear and useful chapter of 17 pages on the theories of solution and some of their applications to analytical chemistry. A note on the capacities of beakers, referred to in the text by numbers, will be appreciated. The paragraphs on temperature of calibration have been rewritten. Of the first edition as an introduction to the principles and practice of quantitative analysis, the present reviewer wrote two years ago: "It is hardly too much to say that it is difficult to see how a better book could be prepared for this purpose than the one before us." After the practical demonstration of two years' use of the book with his classes, his opinion is unchanged, and the additions in the present edition increase the value of the book.

JAS. LEWIS HOWE.

INORGANIC CHEMISTRY ACCORDING TO THE PERIODIC LAW. By F. P. VENABLE AND JAS. LEWIS HOWE. Easton, Pa.: The Chemical Publishing Co. 1898. v+266 pp. 12mo. Price, $1.50.

Professor Venable's studies on the development of the Periodic Law have made so firm an impress on his mind that he has prepared a text-book for beginners in inorganic chemistry which takes the Periodic System as a guiding principle. The professor in the University of North Carolina has associated with him another experienced teacher in the person of Professor Howe, of the Washington and Lee University, and the two have produced a very systematic and accurate work quite up to date. In the hands of enthusiastic teachers the book cannot fail to prove useful in classes, especially if oral explanations supplement the concise and dogmatic statements. Whether beginners in chemistry are competent to appreciate the beauties of the Periodic System before they have learned something of the nature of chemical bodies in general, can be best determined by using the volume; but in any case the study of the terse introduction can be repeated after having read the first fifty or sixty pages. As the distinctive feature of this text-book is the order in which the elements and their compounds are treated, this review will endeavor to do it justice. After giving the history, methods of preparation, and the salient properties of hydrogen, as "the standard element," the elements of the negative subseries of Group VII of Mendeléeff's table are considered; this subseries includes fluorine, chlorine, bromine, and iodine.

Then follow the elements of the negative subseries of Groups VI and V; of Group IV both the positive and the negative series are included; of Group III, chiefly rare elements, only boron and aluminum are discussed; of Groups II and I both series are included. Then Group VIII is taken up, embracing the iron metals and the platinum metals. Part III is devoted to the hydrogen compounds of the elements and under the caption "Hydrids of Group VI" the student first makes the acquaintance of water. Part IV is devoted to halides, and Part V to oxides and sulphides, in which the student is introduced to carbon dioxide, lime, soda, nitrogen oxides, and sulphur oxides, including the important body sulphuric acid. Near the close of the volume there is a summary of the laws of constant proportion, of interproportionality, and of multiple proportions. Part VI deals with binary compounds of Groups V, IV, and with alloys.

The groups of the Periodic System, it will be observed, are discussed in the reverse order in which they appear in Mendeléeff's table, and the positive subseries are not taken up until after the negative. This inversion has been found necessary, probably, to avoid placing before the students the metals (sodium and associates, magnesium and associates, etc.), before the learner has made the acquaintance of the important bodies in Groups I and II (chlorine, bromine, iodine, oxygen, and sulphur). The necessity of consistently treating the elements in the order assigned to them by the Periodic Law leads to some curious results; thus the student finds himself studying selenium and tellurium before he has learned the most simple facts about the atmosphere; and in the same way tungsten, uranium, vanadium, columbium, and tantalum are met with before water. The oxides being in a section by themselves, are separated from the metals of which they form important compounds; thus it happens that between the account of the metal calcium and that of lime there are no less than eighty-six pages, and between lime and limestone there are twenty pages additional. Again the process of smelting iron is explained in connection with the description of the metal, just 150 pages before the characteristics of the oxides of the metal are given.

More attention is given in this book to the comparatively rare elements than is usual; thus more space is given to titanium and germanium than to all the oxides of iron, and the elements molybdenum, tungsten, and uranium, with their compounds, occupy more space than calcium and its compounds in the several sections where they appear.

The book is clearly printed and quite free from typographical errors. The spelling recommended by the American Association for the Advancement of Science has been adopted only in part. Professor Howe, one of the committee on spelling and pronunciation, does not seem to have persuaded his colleague to accept the only rational orthography "sulfur."

Students using this volume will certainly not be misled and will become impressed with the importance of the Periodic Law.

H. CARRINGTON BOLTON.

COMMERCIAL ORGANIC ANALYSIS. VOL. II, PART I. BY ALFRED H. ALLEN, F.I.C., F.C.S., with revisions and addenda by the AUTHOR and HENRY LEFFMANN, M.A., M.D., Third Edition. Philadelphia: P. Blakiston's Son and Co. 8vo. 387 pp. Price $3.50.

The second edition of Volume II of Mr. Allen's valuable work appeared in 1886 and revision at this time was badly needed owing to the rapid advances which had been made in organic analysis. On this account the revision is quite thorough, almost every page and paragraph having been changed to meet the modern requirements. It has also been deemed necessary to divide the volume into two parts to avoid an unwieldy bulk and we now have before us, Part I.

The author and reviser have been compelled to cooperate at such long range, and the demand for the book has been so pressing that Dr. Leffmann has seen fit to assume the responsibility for any statements that do not meet the approval of the author and for any errors which may have crept into the book.

The work is exceptionally well done in every respect and reflects great credit upon the author and the reviser.

This part of Vol. II treats of the fixed oils and fats, glycerine, nitroglycerine, dynamites and smokeless powders, wool fats, dégras, etc. It contains also a list of corrections of the few errors found in Vol. I. Part II, which is now in press, will treat of the hydrocarbons and their immediate derivatives.

The most important additions made to the subjects treated in the volume before us, are: The bromine thermal method, methods for determination of glycerol, acetyl number, tests for oxidation of oils, composition and official methods for the examination of dynamites and smokeless powders, dégras and cloth oils.

Mr. Allen has added to the work some valuable tables giving the sources, specific gravities, solidifying-points, saponification-equivalents, iodine absorption, general characteristics and chief applications of the principal fats, oils, and waxes of commercial or scientific interest.

WM. L. DUDLEY.

BOOKS RECEIVED.

Concentrated Feed Stuffs. Bulletin No. 56. Hatch Experiment Station of the Massachusetts Agricultural College. November, 1898. Amherst, Mass.: Carpenter & Morehouse. 24 pp.

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Very truly yours
Charles E. Munroe

VOL. XXI. [APRIL, 1899.] NO. 4.

THE JOURNAL

OF THE

AMERICAN CHEMICAL SOCIETY.

EXPLOSIONS CAUSED BY COMMONLY OCCURRING SUBSTANCES.[1]

BY CHARLES E. MUNROE.

Received February 27, 1899.

ON the sixth of November last the country was startled by learning that an explosion had occurred at the Capitol at Washington which had caused extensive damage to that magnificent and historic building and which, with the ensuing fire, had destroyed some, and jeopardized more, of the valuable archives with which the building was stored. Occurrences of this kind have long had a particular interest for me, and I have found them to recur with great frequency and to cause extensive damage and destruction not only to property but to person. Notwithstanding, therefore, that much that I have to say is well known, it appears to be not inopportune to address you on the subject of "Explosions Caused by Commonly Occurring Substances," omitting entirely from consideration the substances commonly known and used as explosives, and it is possible that this repetition may serve to some extent in preventing these accidents by leading to greater precautions being taken.

From the observations on the phenomena accompanying the

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[1] President's address read before the New York meeting of the American Chemical Society.

combustion of solids it is well understood that the speed of the combustion is greatly accelerated by comminuting the combustible, and mixing it intimately with the supporter of combustion and it is also well recognized that many explosions are due solely to very rapid combustion, yet it is only within comparatively recent times, and since manufacturing operations have come to be carried on upon a very considerable scale, that we have had it strongly demonstrated that ordinarily combustible solids might, when finely divided and mixed with air, give rise, on ignition, to most violent and disastrous explosions, and it seems especially notable that the first well-demonstrated cases of this kind should have arisen from the apparently harmless operations attending the grinding of grain, and the more particularly as flour is not looked upon as a very readily combustible substance when compared with other commonly used solids.

Among the many instances of this kind which we have now on record we will cite that which occurred on the 9th of July, 1872,[1] when the inhabitants of Glasgow were startled by the report of an explosion which was heard to a considerable distance, and which was found to have occurred in some very extensive flour-mills, the front and back walls of which were blown out, while the interior was reduced to ruins, and speedily enveloped in flame which destroyed the remaining buildings. Several persons were killed, and a number of others were severely burned, or injured by the fall of masonry.

On May 2, 1878, a similar disaster occurred in the enormous flour-mills in Minneapolis, but in this case it was observed that the explosion which originated in the Washburn mill was communicated by flame successively to the Diamond mill and to the Humbolt mill. As a consequence of these explosions the walls of these mills, which were solid masonry, six feet thick at the base, were razed to the ground, sheets of corrugated iron roofing, two by six feet in area, were projected to a distance of more than two miles, a wooden building fifty feet from the center of the explosion was blown open, stout plate glass windows one-fourth of a mile away were torn out bodily, sash and all, and projected into the street, an immense volume of smoke and flame was projected to an estimated height of 600 to 800 feet, and finally

[1] Abel: Roy. Inst., March 12, 1875.

persons by the edge of the adjacent river, observed a displacement of water, producing a wave estimated to be eighteen inches high, before they heard the report of the explosion. The concurrent testimony of persons employed in the mills and of the experts who were called proved the absence in each case of any of the so-called explosive substances on the premises, and that the boilers had not burst, and from the facts brought out the origin was conclusively traced to the striking of fire by a pair of millstones, through the stopping of the "feed," and the consequent friction of their bare surfaces against each other, with the result that the mixture of air and fine flour-dust surrounding the millstones became ignited.

This ignition alone would not suffice to develop any violent explosive effects; for similar ignitions which have been not infrequently observed in small mills, where they have been caused by the stones "striking fire" or by the incautious use of a burning lamp near the millstones, or the meal-spout attached to them, have not been attended by any serious results. But in an extensive mill, where many pairs of stones may be at work at one time, each pair has a conduit attached, which leads to a common receptable called an exhaust-box; into this the mixture of air and very fine flour-dust which surrounds the millstones, is drawn by means of an exhaust fan, which is sometimes aided by a system of air-blowers. The fine flour is allowed to deposit partially in this chamber or exhaust-box, and the air then passes into a second chamber, called a stive room, where a further quantity of dust is deposited. It follows that when the mill is at work, these chambers and the channels are all filled with an inflammable mixture of the finest flour-dust and air, and that the ignition of any portion of the inflammable mixture, will result in the exceedingly rapid spread of the flame throughout the whole, and will thus develop an explosion. The violence of such explosions depends much upon the details of construction of the exhaust-boxes and stive rooms, and upon the dimensions of the channels of communication; it must obviously be regulated by the volume of the inflammable mixture through which the fire rapidly spreads, and upon the degree of confinement. In the case of the catastrophe at Glasgow, the production of a blaze at a pair of millstones was observed to be followed by a crackling noise as the flame spread rapidly through the conduits leading to the exhaust-box upon an upper floor, and a loud report from that direction was almost immediately heard. Professors Rankine and Macadam, who carefully investigated the cause of this accident, report[1] that other flour-mill explosions, which they had inquired into, had been observed to have been attended by a similar succession of phenomena to those noticed upon this occasion. The bursting open of the exhaust-box by a similar though less violent explosion, attended by injury of workmen, the blowing out of windows and loosening of tiles, appears to have taken place on a previous occasion at these particular mills. In the last and most disastrous accident, however, the more violent explosion appears to have been followed by others, the flame having spread with great rapidity to distant parts of the mills through the many channels of communication in which the air was charged with inflammable dust, resulting from the cleansing and sifting operations carried on in different parts of the building, and rapidly diffused through the air by the shock and blast of the first explosion.

In the experimental investigation of the Minneapolis explosion by Professor S. F. Peckham[2] it was shown that compacted masses of flour which had become heated and charred, ignited readily and smouldered but were inflamed only with considerable difficulty, though the atmosphere of the conduit from the stones, through which a strong current of air is being continually drawn and which is filled with a dense cloud of very fine particles of flour heated to a maximum temperature of 140° F., could be inflamed with comparative ease. White-hot wires and glowing charcoal were incapable of producing this inflammation but only burned the particles in actual contact with them, and the only means by which the mixture, in the best proportions, could be made to burn explosively was by contact with flame.

The danger in the process was found to arise from the friction of the stones, heating the last portion of the grist that remained between them to a temperature sufficient to char it, or to convert it into a substance resembling tinder, which would readily ignite from a spark produced from the stones striking together.

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[1] Abel: Roy. Inst., March 12, 1875.

[2] *Am. J. Sci.*, 16, (3), 301-306 (*1878*).

Although this burning mass could not inflame the dust-laden atmosphere, it did ignite wood, which a strong draught of air readily forced into a blaze. Under the conditions described, with a draught of air passing through the dry stones strong enough to convey the pellets of smouldering tinder into the wooden conductor, an explosion was a necessary consequence.

Knowing the chemical composition of flour, we may calculate approximately the mechanical work which a given mass of flour can perform, and find that the contents of an ordinary sack, when mixed with 4000 cubic feet of air, will generate force enough to throw 2500 tons mass to a height of 100 feet. If we now consider the many tons of flour there must have been in a mill such as the Washburn "A," where as much as 1000 pounds of dust per day were collected from a single pipe, we can readily comprehend how such great destruction could be wrought.

It is to be regretted that the experts, who duly considered all the circumstances, concluded that while by suitable precautions the frequency of these flour-mill explosions may be diminished, and the extent of the damage inflicted may be very much restricted, the nature of the operations is such that these explosions cannot be altogether prevented.

Since mixtures of wheat-dust with air have proved to be so explosive we should naturally expect that analogous solids would form similar explosive mixtures with air, and as a fact we have recorded explosions of oatmeal in the Oliver mill in Chicago, of starch in a New York candy factory,[1] of rice in rice mills, of malt-dust in breweries, of spice-dust in spice mills, together with numerous instances of sawdust explosions, the more prominent being those which occurred in the Pullman car shops and at Geldowsky's furniture factory in Cambridge, Mass., still we would scarcely look for an explosion from such a cause in a soap factory. Yet a violent explosion occurred in 1890, in a Providence soap-works in which the finely powdered saponaceous substance known by the trade name of "soapine" was being prepared and the coroner held in his finding that the explosion through which such injury was inflicted was caused by the ignition of soapine dust. Experiments made in this connection

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[1] L. W. Peck: "Explosions from Combustible Dusts," *Popular Science Monthly*, 14, 159-166 (*1878*).

showed that this substance will explode under certain conditions with more violence than flour and apparently with the production of more heat.

The most unusual case of dust explosions, however, with which we have met, was that of finely powdered metallic zinc which occurred at the Bethlehem Zinc Works in 1854. At that time Col. Wetherill devised a plan for utilizing the "blue powder" which is the finely divided metallic zinc that is deposited in the prolongation of the condenser by swedging the powder into blocks and piling these blocks one above another in a furnace where they were melted down and run into spelter. The workman in charge sought to facilitate the process by feeding the uncompressed powder directly into the furnace but on trying to do so an explosion followed the loading of the first shovelful and with such violence that the workman was blown from the top of the furnace, and the blade of the shovel was driven into the roof of the building.

In pharmacy and the arts, substances have been made either knowingly or accidentally from mixtures of combustible substances and supporters of combustion which have given rise to accidents such as those from the parlor match and the chlorate troches,[1] or from sodium peroxide and sodium bisulphite mixtures as in the Whitecross Street explosion,[2] and the latter class of mixtures are to be particularly dreaded as the chemical action and subsequent explosion may be incited not only by contact with fire but also by contact with water. Cavazzi[3] points out that mixtures of sodium nitrate and hypophosphite detonate on heating, while Violette[4] proposed to use a mixture of sodium nitrate and acetate as a substitute for gunpowder, and these are but a few among the many explosive mixtures which may be compounded.

Still another source of danger arises from the production and use in laboratories, and frequently in common life, of chemical substances which are explosive *per se* though not generally recognized as such and we have records of accidents, among others, from bleaching-powder,[5] from erythryl nitrate, which has lately

[1] *U. S. Naval Institute*, 11, 774 (*1885*).

[2] *J. Soc. Chem. Ind.*, 13, 198–200 (*1894*).

[3] *Gas. chim ital.* (*1886*).

[4] Berthelot : Sur la force de la poudre (3), 2, 315.

[5] Rept. H. M. Insp. Exp., p. 47 (*1897*).

come into use in the treatment of Angina Pectoris,[1] from ammonium nitrate[2] and there are many others such as the organic nitrates,[3] nitroso compounds,[4] diazo bodies,[5] diamides,[6] hydrazoic acid and its derivatives,[7] hydroxylamines,[8] chlorates,[9] carbonyl compounds,[10] permanganates,[11] peroxides,[12] chlorides,[13] and iodides,[14] occurring in the laboratories and used to a varying extent in the arts that are so unstable as to give rise to serious accidents if incautiously handled. We may notice that so well known a compound as the cupric ammonium nitrate, a body which is often formed in the course of analysis, was deemed by Nobel to possess such value as an explosive that he took out patents for its use in blasting.

The liquid state conduces more particularly to accidents taking place since bodies in this state are liable to escape from their receptacles and to be found in unexpected places. If combustible, when mingled with the atmosphere or when saturating oxidizing agents, they burn with extreme rapidity and produce very violent effects. When such liquids give off vapors at the ordinary temperatures or those prevailing during use, the danger is very materially increased as such vapors are more vagrant and, through diffusion, readily mingle with the atmosphere. These properties are especially characteristic of many of the products obtained from coal-tar and from petroleum; bodies whose cheapness, abundance, and special adaptability have led to their extended use for domestic heating and lighting and for many purposes in the arts, but which have, because of this wide-spread use and in consequence of their possessing the properties named, been the cause of an enormous number of casualties. Dr. C. F. Chandler[15] showed that much of the danger attending the use of

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[1] Rept. H. M. Insp. Exp., p. 50 (*1898*).

[2] *J. Chem. Soc.*, 683 (*1882*).

[3] *Compt. rend.*, 109, 92–95 (*1889*).

[4] *Compt. rend.*, 108, 857–859 (*1889*).

[5] *Ann. Chem.* (Liebig), 121, 257 (*1860*).

[6] *J. prakt. Chem.*, 30, 27, 107.

[7] *Ber. d. chem. Ges.*, 23, 3023 (1890).

[8] *Rec. d. trav. Chim. Pays. Bas.*, 10, 101 (*1891*), and *J. Chem. Soc.*, 54, 425 (*1888*).

[9] *Compt. rend.*, 105, 813 (*1887*).

[10] *Ber. d. chem. Ges.*, 18, 1833 (*1885*).

[11] *J. Chem. Soc.*, 54, 250 (*1888*).

[12] *Compt. rend.*, 106, 100 (*1888*).

[13] *Bull. Soc. Chim.*, 50, 635–638.

[14] *J. Chem. Soc.*, 56, 766 (*1889*).

[15] "Petroleum as an Illuminator," Rept. N. Y. City Board of Health for 1870.

these oils in lamps could be avoided by the elimination of the paraffins of low boiling-points and though not the pioneer, yet largely through his active efforts and the agitation which followed them, this principle has properly become widely embodied in legislation. This view as to the source of danger was confirmed by the experiments of Newbury and Cutter,[1] who found that all the paraffins below nonane formed explosive mixtures with air at the ordinary temperatures, notwithstanding that the boiling-point of octane is 124° C., and that the limit of a safe oil as fixed by the "flashing test" defined by the New York State statutes is reached only in decane. Yet this last-named compound formed a violently explosive mixture at the legal flashing temperature if but a small quantity of the liquid was placed in the copper testing vessel, thus indicating that entire safety is not assured in its use and that accidents might occur when it is used in lamps so constructed that the oil chamber becomes highly heated. Dewar[2] holds that the relative volatility of petroleum oil is a subject which is not sufficiently known and appreciated. By comparing the loss of weight during twenty-four hours of oils exposed in shallow vessels under similar conditions he found at 66° F., an American water-white oil of 106° flash-point lost 20.4 per cent., an oil of 75° flash-point lost 27.4 per cent., and a Russian oil of 85° flash-point lost twenty-eight per cent.

In observations that I have made it was very apparent that the form and material of the containing vessel are most important factors in these volatilization experiments. I have found for instance that a given volume of gasoline placed in an uncorked vial and exposed to the ordinary atmospheric conditions of a laboratory required ten weeks for complete volatilization when the same volume of the same lot of gasoline placed in an evaporating dish standing beside the bottle volatilized completely in eight hours. The rate of evaporation of the various hydrocarbons under the same conditions has been studied by Boverton Redwood.[3]

A menace in the use, storage, and transportation of these liquids rests in the rapidity with which their vapors diffuse through

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[1] *Am. Chem. J.*, 10, 356–362 (*1888*).

[2] Rept. H. M. Insp. Exp., 21, 55 (*1897*).

[3] "Detection of Inflammable Gas and Vapor in the Air," Frank Clowes, p. 191 (*1896*), London.

the air and form an explosive train which, reaching out to a source of ignition, flashes back with extreme rapidity through the entire train and to its point of origin. Sir Frederick Abel cited an instance of this which[1] happened at the Royal College of Chemistry in 1847 when a glass vessel in which benzene was being converted into nitrobenzene broke and allowed the warm liquid to escape and flow over a large surface. Though the apartment was thirty-eight feet long, thirty feet wide, and ten feet high, and the only ignited gas-jet was at the end of the room most remote from the glass vessel, yet in a very brief space of time after the vessel broke a sheet of flame flashed from the gas-jet and travelled along the upper part of the room to the point where the fluid lay scattered.

He also cites the explosion of benzoline at the mineral oil store in Exeter in 1882. The storerooms were arched caves in the side of a bank facing a canal and separated from it by a roadway about fifty feet wide. There was a standing rule forbidding any light being taken to any of these storerooms when they contained petroleum spirit, but on the day in question it was desired to remove some of the benzoline in the early morning and the foreman visited the storerooms before daylight to make ready for the work. Forgetful of the rule he carried a lighted lantern, which he placed on the ground some twenty-seven feet away from the cave, and was proceeding to open the door when he observed a strong odor of benzoline and almost immediately noticed a flash of flame proceed from the lantern to the store and had barely time to turn to escape when an explosion took place which blew the doors and lantern across the canal and inflamed the spirits in the storerooms.

Of course the distance that these vapors will travel will be determined by the circumstances of each individual case but in the case of the fire at the L. & N. W. R. R. Co's gas factory in February, 1897, through which the hydrocarbons in a cylinder that was being rolled across the yard about the works became ignited, the nearest source of ignition was found in the boiler fires which were sixty feet away.[2]

Conditions such as these are more likely still to obtain when

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[1] Roy. Inst. of Great Britain, March 13, 1885.

[2] Rept. H. M. Insp. Exp., 22, 57. (*1898*).

these inflammable and volatile substances are stored in enclosed spaces such as the hold of a vessel during transportation and they have been the cause under these conditions of many frightful accidents. As an example of these we have the case of the explosion on November 21, 1888, on the petroleum-laden ketch "United" at Bristol, England, through which the docks were blown up, three men killed and several injured, the glass in the windows shattered for a radius of upwards of 300 feet and extensive damage done by fire.

The accident was made the subject of a special report by Col. V. D. Majendie[1] which contains the results of his investigation and the experiments by Dr. Dupré and Mr. Boverton Redwood, from which it appears that the material on the "United" was "deodorized naphtha" in forty-two gallon barrels; that the average annual leakage on petroleum oil in barrels amounted, in 1874, to eight per cent. and on petroleum spirit to double this quantity, and that though there has since been a great improvement in the treatment of the barrels it is still very large; that one volume of the liquid gives 141 volumes of vapor at ordinary temperature having a specific gravity of 3.5 to 3.8; that one volume of the liquid will render 1,6000 volumes of air inflammable, 6000 most violently explosive, 5000 strongly explosive, and 3000 scarcely explosive but combustible. The naphtha vapor alone or when mixed with air in the best proportions was not ignited by a shower of sparks from flint and steel, by a stream of sparks from fireworks of various kinds burning without flame, by incandescent match ends, or by incandescent platinum heated by electricity to a red heat. Even red-hot coals held over and sometimes falling upon a small quantity of the spirit spilled on a wooden floor failed usually to ignite it, and the cause in those cases in which ignition did take place in these red-hot coal experiments was uncertain as there was a fire burning in a near-by room. Ignition was, however, certainly effected by the application of a flame or by contact with a platinum wire approaching incandescence.

The "fireworks" test makes a striking lecture experiment, especially the one devised by Mr. Redwood with "vesuvians" or incandescent cigar lighters. For this purpose he attaches

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[1] Eyre and Spottiswoode, London (*1889*), 30 pp.

two, of the glowing variety, to a wire so that the tip of one will be in contact with the base of the head of the other. The latter is lighted and when it ceases to flame and only glows, the mass is thrust into the explosive mixture, where it remains with the combustion progressing from tip to base and base to tip without other effect until, when flame bursts from the tip of the second vesuvian, the vaporous mixture surrounding it is ignited and an explosion ensues.

Col. Majendie has properly called attention in this report to the fundamental distinctions between the danger arising in the transportation of a cargo of dynamite and one of petroleum spirits since in the former case an explosion does not take place until fire is brought to the dynamite, while in the latter case the dangerous vapors will travel to a fire at a considerable distance and even through intervening bulkheads.

For this reason mixed cargoes, of which volatile inflammable liquids and explosives constitute a part, are particularly dangerous as was long since shown in the explosion of the canal boat "Tilbury" in Regent Park in 1874, having on board five tons of gunpowder and four barrels of benzoline and also having a small fire burning in the after cabin some thirty-five to forty feet from the forehold in which the petroleum was stored. Notwithstanding that the cargo was covered with tarpaulins, and that there was an intervening bulkhead, the vapors reached the fire and a most devastating explosion followed. The cargo was thus made up in spite of a similar disastrous experience from similar causes on the "Lottie Sleigh" at Liverpool in 1864[1] and neither of them have proved a sufficient warning to altogether prevent subsequent reckless disregard of all dictates of common prudence.

Yet because of these experiences attempts have been made in some instances where small lots of spirit were taken by vessels to avert disaster by carrying them as deck loads, but the experience on the "Solway" which carried twenty-four barrels of this article on the main deck before the poop shows that this does not insure security, for, meeting with heavy weather the casks broke adrift, their vapors reached the galley or cabin fires and the vessel, with nineteen persons, was lost.

Even where great precautions are taken to prevent accidents

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[1] Abel: *Loc. cit.*

they not infrequently occur from inflammable substances being met with in unexpected places or being introduced surreptitiously in admixture with harmless bodies. Nowhere perhaps is more care taken in this respect than on passenger steamships, and in the naval service yet eighteen years ago a series of accidents occurred on board English ships, the cause of which was for a time veiled in mystery, and which, in the then existing state of feeling consequent on the dynamite outrages, aroused the gravest apprehensions.

In June, 1880, a violent explosion took place, without any warning or apparent cause, in the forepeak of the Pacific Steam Navigation Co.'s steamer "Coquimbo" shortly after her arrival in Valparaiso. Several plates were blown out of the bow and other structural damage was inflicted while the ship's carpenter, who was the only person who could have thrown any light on the cause of the accident, was killed.

This explosion was followed on April 26, 1881, by a much more serious one on the man-of-war "Doterel" (while at anchor off Sandy Point in the Straits of Magellan), through which eight officers and 135 men lost their lives and the vessel was destroyed. In May of the same year an explosion of a trifling character happened on H. M. S. "Cockatrice" in Sheerness Dockyard, while in November, one, which was sufficiently severe to kill two men, dangerously wound two more (one fatally) and injure six others, besides doing much damage to the ship, occurred on H. M. S. "Triumph" then at Coquimbo.

The first suggestion as to the real cause of these accidents was obtained in the investigation of that on the "Cockatrice," when it was developed that, just previous to the explosion, a man went into the storeroom with a naked light which he held close to a small can, that was uncorked at the time, and which contained a preparation recently introduced into the naval service (as a "drier" for use with paint) under the name of 'xerotine siccative,' and that this largely consisted of a most volatile petroleum product. As it had been issued without knowledge of this fact, instructions were at once sent out by the Admiralty directing that it should be stored and treated with the same precautions as turpentine and other highly inflammable liquids or preparations; and these instructions had but recently reached the "Triumph" when the accident narrated happened to her. Inquiry here developed the fact that the explosion originated in the paint room through bringing a lantern to a compartment in which a leaky can of the siccative had been stored, and following up this clue the explosions on the "Coquimbo" and "Doterel" were fully and definitely proved to have been due to the presence, on board, of this same substance, while experiments with the material showed that it was capable of producing all the destructive effects observed, except, perhaps, in the case of the "Doterel", where, from the two reports noted and the other resemblances to the Regent Park explosion, there was but little doubt that the powder magazine was also exploded.

Such accidents were not, however, confined to British vessels for on October 13, 1891, while the U. S. S. "Atlanta" was going to the rescue of the wrecked "Tallapoosa", an explosion occurred on the "Atlanta" which caused her immediate return to New York. I was at once ordered by the secretary of the navy to proceed to New York and investigate the accident.

I learned that while the "Atlanta" was laboring in a heavy sea she sprung a leak through the hawse pipes and the forward collision compartment began to fill with water; that a handy-billy was rigged to pump the compartment; that about midnight the suction-pipe became plugged, and that on lowering a common lantern into the compartment an explosion ensued severely injuring two men, slightly injuring four others, and bulging the steel collision bulkhead. I found that the collision compartment had been used as a storeroom for paints; that among them were spar and damar varnishes and Japan dryer each of which gave off inflammable vapors at ordinary temperatures; that the packages were sealed in a very insecure manner; and that as this compartment filled and the vessel tossed, the cans were opened and their contents churned up so as to readily form explosive mixtures with the air. I learned further that on June 15th previous, a fire and explosion had taken place on board the U. S. S. "Philadelphia" in close proximity to her powder magazine, and that another had occurred on the U. S. S. "Bennington", all being evidently due to the same material.

But notwithstanding these vigorous lessons the tale continues and on April 14, 1896,[1] a "petroleum accident" occurred on

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[1] Rept. H. M. Insp. Exp., 21, (*1897*).

board the Cunarder S. S. "Servia" when a party of men were engaged in painting the inside of a water-ballast tank. The tank, which was three feet six inches deep, was divided into sixteen compartments with eighteen inches aperture between each. The furthest compartment was being painted at the time and it was necessary to crawl through fifteen of the small apertures to reach it. The paint used was styled patent bitumastic solution, and one of the survivors testified that it took him four or five minutes to reach the compartments, ten minutes to do the painting, and four or five minutes to return, and that he could not stoop down any longer as it made him dazed and queer in his head. All the witnesses testified that the use of the solution in confined spaces made them drunk and delirious if they remained any length of time at work. This is a well-known effect of the lighter petroleums, and it is not surprising that the solution was found to consist of coal-tar dissolved in crude oil, having a flashing-point of 45° F. Abel, and containing so much volatile matter that one gallon spread over a large surface would render forty-eight cubic feet of air inflammable.

Notwithstanding this the workman went into this inner compartment, which was already partly covered with the freshly-laid solution and containing a partly filled bucket of it, with a lighted candle. Sometime having passed without hearing from him another workman went to his assistance and found the place on fire and the man burned and delirious. He was so delirious as to fight against coming out and it took an hour and a half with assistance to get him through the apertures and up the manhole, and he afterwards died in the hospital from the effects of the disaster. Even while writing this we learn from the local press that a fire preceded by an explosion, due to the use of bitumastic solution, occurred at the Central Market House, Washington, D. C., on November 16, 1898.

The notorious "Hair Dressers' Accident" of June 26, 1897, through which Mrs. Samuelson was fatally injured in London, by the ignition of a petroleum hair-wash which was being used as a shampoo, illustrates anew the manifold uses to which these hydrocarbons are being put and it brought out strongly the belief of competent authorities like Lord Kelvin that these substances could be ignited by frictional electricity,—a theory which had been offered before in explanation of accidents in which there was no other apparent source of ignition.

The wide-spread distribution of these spirits in the hands of retailers, or as used for carburetters in isolated vapor lighting plants and as employed in the arts for solvents, cleansing agents, and for other purposes has led to their accumulation, through leakage or by being discharged after use, in low places such as cellars, cisterns, wells, sewers, and the bilges of ships where they have remained, in some instances for long periods of time, unknown and unnoticed, their origin even being completely forgotten and untraceable, until, when, in the course of events, these out-of-the-way places have been reentered, these bodies have given rise to accidents. It is a well-known precaution of the past before entering a well or cave to test its atmosphere for carbon dioxide by means of a naked candle but this very method of procedure has, since the introduction of petroleum, been the cause of accidents and to be assured of security we must now remove and test the air before entering.

The extended consumption of naphtha for carburetting water-gas and the ease with which it is conveyed through pipes has resulted in the use of systems of pipe lines in our cities to carry the oil from the transportation lines or store tanks to the works. Such a line was laid in Rochester, New York, and on December 21, 1887, it gave rise to an explosion which killed three men, seriously injured twenty, destroyed three large flour-mills, tore up the streets for a considerable distance, and inflicted an estimated loss of $250,000. This pipe line, which was made of three inch wrought iron pipe, one and one-half miles in length, had been in successful use for six years, the spirits being pumped through it every two weeks in lots of from 12,000 to 15,000 gallons each. From the Appeal Book *in re* Ann Lee *vs* the Vacuum Oil Co., Rochester, 1889, we learn that the conveyance of the naphtha was complete on December 7; on December 8, the contractors constructing a sewer exposed a section of the pipe line, for several feet, and in blasting beneath it a piece of rock struck the pipe with sufficient force to bend it up nearly nine inches at the point struck and to separate it at a joint further on underground and closely connected with a sewer; that on the day fixed for the next delivery, December 21, the Oil Company, being unaware of the then existing conditions, pumped the full supply into the pipe none of which reached the gas works but on the contrary found its way, by the broken joint, into the sewers and was thus distributed over the city ; that the pumping of the oil began at 12.15 P.M. ; the odor was noticed shortly after 1 P.M. coming from a sewer at a point nearly a mile distant from the break ; the first explosion occurred at this point at 3.20 P.M. and immediately extended westward back to the break and eastward to the outlet of the sewers, tossing up manhole plates, uplifting roadways and overturning buildings ; that the explosive mixture was ignited by a fire under a steam boiler ; and that this vapor found its way from the sewer to the fire through an untrapped water-closet at a point where exhaust steam was being injected into the sewer.

At the trial, Mr. F. L. King, p. 173, stated that crude naphtha, flashing-point 13° F., percolated through earth six times as fast as water at the same temperature, his several experiments being made with temperatures varying for the liquids from 38° F. to 60° F., and for the earths from 32° F. to 60° F. Mr. George B. Selden, p. 178, found the mixture of naphtha and air in the best proportions to give, on explosion, a pressure of 140 pounds per square inch, while coal-gas and air in the best proportions gave 160 pounds per square inch, and that the ignition-point of the naphtha mixture was 950° C., while that of the coal-gas mixture was 800° C.

I have already referred to the means taken for insuring the removal of the more volatile hydrocarbons from domestic kerosene, a subject which has been very exhaustively treated by Rud. Weber.[1] It has, however, been seriously stated that the lighter oils such as benzoline or naphtha might be rendered safe for use in lamps by adding alum, sal ammoniac, or camphor to them, and many innocent persons have suffered in consequence of their belief in the efficacy of these substances. Some years since[2] I tested the effect of these bodies by determining their solubility in benzoline ; the flashing-points of benzoline and commercial kerosene when treated with these bodies and when in their original state ; and also the readiness with which mixtures of the oils, in the two conditions, with air could be exploded.

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[1] Dingler's *poly. J.*, 241. 277 and 383 (*1881*).

[2] *Proc. A. A. A. S.*, 33, 174 (*1885*).

The results showed that alum and sal ammoniac were practically insoluble in the oils and produced no effect whatever upon them; that the camphor was soluble, one gram of benzoline dissolving about one and five-tenths grams of camphor; that an equal weight of camphor raised the flashing-point of a kerosene 12°; but that on the other hand the vapor of this camphorated kerosene, when mixed with air, had a lower point of ignition and hence exploded with greater readiness than the original kerosene.

What is true regarding the use, storage, and transportation of petroleum products holds for other easily volatile liquids. Prof. Thomas Graham in his report[1] on the cause of the loss of the "Amazon" on January 4, 1852, pointed out clearly the danger in transporting turpentine, while the destruction of the "Livadia" of Liverpool, May 11, 1891, carrying a cargo of carbon disulphide, emphasizes the hazard attending this substance, for this heavy and very mobile liquid gives off quite rapidly, at ordinary temperatures, a vapor which is 2.64 times heavier than air, and which not only readily collects at the bottom of any space in which it is produced but flows in a stream like water.

One of the more striking characteristics of the mixture which this vapor forms with air is its low point of ignition. The tiniest spark, a cinder after it has ceased to glow, or the striking together of two pieces of iron without sparking are sufficient to determine its ignition. This property may be exhibited by plunging a glass rod heated to 231° C. (450° F.) (a temperature at which it can be touched with the bare hand), into the mixture.

The use of ether, alcohol, acetone, and aldehyde with nitroglycerine and guncotton for the manufacture of smokeless powders and of the esters as solvents for pyroxylin in the making of the varnishes that are largely used in household decoration are some of the more modern forms of hazard, while the explosion at the Hotel Endicott in New York and at Newark, N. J., indicates what may be expected from the more extended use of liquefied air and liquefied acetylene.

Although Dr. John Clayton, the Dean of Kildare, in the sixteenth century effected the destructive distillation of coal and

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[1] "Spontaneous Combustion and Explosions Occurring in Coal Cargoes," Thomas Rowan, p. 40 (*1882*).

collected and burned the gas from it,[1] it was not until 1792 that William Murdock devised the means for utilizing the substance and erected a plant, at Cornwall, England, with which to light his house and office, and after several years of active agitation by the energetic promoter, F. A. Winsor, that in 1810 an Act of Incorporation was obtained for the London and Westminster Gas-Light and Coke Co., and the first installation on a large scale for lighting the streets of a city and supplying the public begun, and through the ingenuity and resources of Samuel Clegg, the engineer, the devices were invented or assembled by which the practical manufacture, storage, distribution, and use was successfully accomplished.

From this source the use of gas for lighting and heating extended over the world reaching New York in 1834 and bringing in its train comfort and cheer; increased security and added power to man so long as the substance was confined to its proper channels and used in proper devices but carrying also the possibility of working harm if the vigilance of its keepers was relaxed and it escaped from bounds; therefore beginning with the explosion at the lime purifier of the Peter Street Station, London, in 1814, through which Mr. Clegg was injured and two nine-inch walls thrown down we have a vast array of explosive accidents originating in the ignition of mixtures of illuminating gas with air.

Owing to the circumstances attending some of these explosions there has arisen a vulgar opinion that illuminating gas is an explosive; in fact in a recent case[2] counsel cited opinions of courts deciding "gas" to be explosive; yet every chemist knows that it is not explosive *per se* and that it cannot even be made to ignite unless in contact with air or other supporter of combustion.

While we know the truth and may be able to demonstrate the fact it is very satisfactory to be able also to cite the results of experience on a large scale. Therefore the following from the *Jour. of Gas-lighting*, Aug. 1, 1871, may be welcome. It appears that at the bombardment of Paris the Governor of the city feared the gas-holders of La Villette would endanger the fortifications.

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[1] Treatise on Coal Gas, William Richards, (*1877*).

[2] *Proc. U. S. Nav. Inst.*, 22, 638 (*1896*).

He was assured that there was not the smallest risk; that if a projectile penetrated a gas-holder and set fire to the gas the latter would only burn out as a jet of flame, and that there could be no such thing as an explosion since the constant pressure would effectually prevent any access of air. Shortly after, a shell pierced the holder at Ivry and lighted the gas. There was a huge jet of flame for eight minutes, the holder sank slowly, and all was over. At La Villette a shell penetrated a filled gas-holder and burst in the interior without igniting the gas. At Vaugirard another shell entered and again there was neither ignition nor explosion.

Many of the accidents from coal-gas and its congeners "water-gas," "producer gas," and "generator gas" have been due to the escape of the gases from the interred pipes and mains from which they have reached sewers, cesspools, cellars, and other enclosed places, for though these gas conduits may be sound and tight when laid, leakage will in time be caused by the corrosive action of materials in the soil, by electrolysis, by fluctuations in temperature, by settlement in filled ground, and by seismic changes.[1] The extent of this leakage from the mains in New York City was discussed in a legislative investigation some nine years ago, and while the chemist of the health department claimed that ten per cent. of the entire annual product or 1000 million cubic feet escaped, the gas companies' representatives denied that more than 100,000,000 feet were lost in each year. W. C. Holmes & Co.[2] give the allowed leakage as five per cent. and the average leakage as ten per cent. while H. Tobey in his paper on "Elusive Leakages for Mains and Services,"[3] which was warmly discussed by the Gas Association before which it was read, shows that the condition still exists, and he gives illustrations showing the danger consequent on leaving abandoned sewers in place.

Owing to the fact that Bunsen, Angus-Smith, Letheby, and Durand-Claye found large quantities of methane, hydrogen sulphide, and sometimes carbon monoxide, in the gases from stagnant sewage decomposing under water, there has arisen a belief that "sewer-gas" is explosive. Simple consideration of the

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[1] Milne: *McClure's Mag.*, 11, 17–27 (*1898*).

[2] "Instructions for the Management of Gas Works," p. 41, Lond. (*1874*).

[3] *Am. Gas-Light J.*, 64, 767 (*1896*).

facts that such stagnation cannot occur in a properly constructed sewer and that such a change does not take place in flowing sewage is sufficient to cast doubt on the existence of such a gas. It has been completely shown by Prof. Wm. Ripley Nichols in his "Chemical Examination of Sewer Air"[1] as the result of his own extended observations, and from the discussion of numerous data by other investigators, that sewer air differs from ordinary air only in containing a larger percentage of carbon dioxide and that "sewer air is neither inflammable nor explosive." The air of vaults and cesspools is, of course, a different thing as the material in these may become stagnant.

It was as early as 1819 that an English patent was granted to David Gordon and Edward Heard, for compressing gas in strong copper or other vessels fitted with ingenious reducing valves for regulating its rate of emission, thirty feet of gas being compressed into a volume of one cubic foot; and gas so compressed in cylinders of two cubic feet capacity were conveyed to the houses of consumers, with which to operate an isolated plant. Sometimes the pressure was sufficient to liquefy the gas and it is interesting to note that it was in the liquid from one of these reservoirs that Faraday discovered benzene.

Naturally the tension of the gas itself tends to rupture the receptacle and many accidents from explosions of this nature have occurred owing to defects in the cylinders, or to the exposure of the filled cylinders to unduly high temperatures, or to shocks; a recent accident that could not be explained in any other way occurred at Albany, N. Y., on December 6, 1893.[1]

With the increased demand for compressed gases of various kinds under high tensions, such as carbon dioxide, sulphur dioxide, ammonia, chlorine, nitrogen monoxide, acetylene, air, and others which are being used or introduced for commercial, scientific, or domestic purposes, there is being developed a continued improvement in the strength and homogeneity of the cylinders so that the danger from this cause is diminishing.

Although Dr. Robert Hare had invented his oxyhydrogen blowpipe in 1801[2] yet in 1834 Gordon and Deville were granted a patent for their calcium or "lime" light. It was expected by

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[1] Rept. Supt. of Sewers, Boston, Mass., 1879.

[2] *Proc. U. S. Nav. Inst.*, 22, 638 (*1896*).

[3] This Journal, 19, 719 (*1897*).

the projectors that this form of light would replace gas, as burned from ordinary burners, for lighting streets, and it caused the holders of gas securities much anxiety, but as we are now aware the device came to be used for geodetic, scientific, and exhibition purposes only.

Where the gases stored in vessels are of an inflammable nature there is an additional risk to that due to the tension of the gas since by admixture with gas or oxygen an explosion occurs on ignition. One source of these accidents arises from the diffusion of one gas back into the reservoir of another gas, but this is entirely prevented by proper regulation of the pressure and size of the orifice. Another arises from confusing the cylinders when filling them and to prevent this the cylinders have been painted different colors. Yet as shown by the fatal accident described by W. N. Hartley[1] this has not prevented the deliberate interchange of the cylinders under the pressing demands of trade, and the usual casualty has followed. Therefore he proposes that the fittings for the two classes of cylinders be made so entirely different that it will be practically impossible to charge the cylinder with the wrong gas and in view of the probable increased use of gas in this form as indicated by Mr. Thomas Fletcher[2] the change should be made. Yet I doubt if it will be, except under compulsion of law, for I have learned in my efforts to introduce safety explosives in this country that the great majority will not secure the assurance of safety if this entails a little inconvenience and the taking of a little more pains.

A more common source of accident has come from impurities introduced in the making of the oxygen as, at Nahant, Mass., where pulverized stibnite was mistaken for pyrolusite, and mixed with the potassium chlorate. Limonsin describes an accident at Cannes in 1880, which attracted unusual attention from the factitious circumstance that the gas was being prepared for the Empress of Russia,[3] and found the cause in the evolution of hydrocarbons from the rubber connecting tube by particles of heated potassium perchlorate carried into it through the turbulence of the reaction; while Prof. C. A. Young gives an account[4] of the explosion at Princeton while filling a steel cyl-

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[1] *Chem. News*, 59, 75 (*1889*).

[2] "On a New Commercial Application of Oxygen." *J. Soc. Chem. Ind.*, 7, 182 (*1888*).

[3] *U. S. Nav. Inst.*, 14, 167 (*1888*).

[4] *Scientific American*, p. 369, June 11, 1887.

inder with oxygen by means of a water-jacketed, steam force pump and finds the cause in oil used for lubricating the pump being sprayed into the gas cylinder so as to form an explosive mixture with the oxygen. He recommends the use of soap-suds as a lubricant in place of oil. Frankland[1] describes a similar instance and gives a similar explanation. Recently my attention has been called to several accidental explosions of oxy-hydrogen mixtures formed in the operation of storage batteries, the detonating gas being fired by the spark formed on breaking connections at the battery.

But of all circumstances under which explosions occur the most awful are those which so frequently happen in mines, for if the miner escapes instant death it too often is but to die from suffocation or worse yet to be entombed and perish from starvation preceded perhaps by insanity.

It has long been known that fire-damp found its way into coal mines, and in 1674 Mr. Jessop communicated to the Royal Society a description of the accident met with by Mr. Michel who penetrated into the gallery of a coal-pit in Yorkshire with a naked torch and was severely burned. It is interesting to note[2] that, when rescued, he declared he had heard no noise though the workmen in the vicinity had been terrified by a tremendous report accompanied by a vibration of the earth. As is to be expected, from what we now know of natural gas, inflammable gases are not confined to coal mines, but, as shown by B. H. Brough,[3] they are met with in metalliferous mines and other excavations also.

The appalling nature of these catastrophes led to efforts being made to at least reduce their frequency if not to prevent them altogether, an extended account of these being given in "Mining Accidents and their Prevention" by Sir Frederick Abel, N. Y., *1889*. It was early recognized that the presence of naked light was a constant source of danger and hence the invention of the safety-lamp by Sir Humphry Davy in 1816[4] was hailed as a most beneficent gift of science, and this was soon followed by the lamps of George Stephenson and Dr. Clauny. When exposed

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[1] *Am. Gas-Light J.*, 5, 289 (*1864*).

[2] Treatise on Coal Gas. Wm. Richards, p. 4, 1877.

[3] School of Mines Quart., 12, 13–22 (*1890*).

[4] *Trans. Roy. Soc.*, 106, 1.

but a short time in an atmosphere rich in gas, and which is moving at a low velocity, these lamps protected the miner; but if allowed to remain for some time in the gas-rich atmosphere the gauze becomes heated to the ignition-point of the gas mixture burning within it. By the introduction of ventilating appliances to remove the gas, the currents of air in the mainways frequently reach a velocity of between twenty and twenty-five feet, and between two airways it may rise to thirty-five feet per second. In breaking down the coal, the confined gas may rush out at a very high velocity it being found by experiment at the Boldon Colliery that the gas may be under as great a pressure as 461 pounds to the square inch. And finally the air and gas may be set in motion at a high velocity by the firing of explosives to bring down the rock or coal, and more especially by a "blown out" shot. Under such conditions the primitive safety-lamps above described failed but protected lamps have been invented which have resisted currents of even fifty feet per second for a brief period, though it is said that these are insecure in certain positions to which they may be tilted in practice and that the glass cylinders are liable to fracture.

Instead of relying upon the safety-lamps for protection a better method of procedure is to test the atmosphere of workings for the presence of fire-damp before allowing the workmen to operate. Various methods have been pursued and these are summarized in "The Detection and Measurement of Inflammable Gas and Vapor in Air" by Dr. Frank Clowes, *1896*, Lond., and he there describes a very ingenious and efficient fire-damp detector which he has devised. This consists of a simple and convenient hydrogen lamp by which one can detect 0.10 per cent. of methane or 0.25 per cent. of coal-gas in air. He attaches a small steel cylinder (weighing about fourteen ounces) charged with hydrogen under 100 atmospheres of pressure to the side of a safety-lamp and leads the gas through a minute copper tube up beside the wick holder of the lamp, there being a reducing valve attached to the cylinder by which to feed the hydrogen to the lamp as desired in order to control the height of the flame.

The lamp is lighted as usual at the oil wick and covered; then, when the atmosphere, which it is desired to test, is reached, the hydrogen is turned on and ignited, the oil flame is pricked out, the hydrogen flame adjusted to a regulation height of ten mm. and the flame observed through the chimney against a black background. If an inflammable gas be present it will produce a pale blue cap about the hydrogen flame and the height of this cap will increase with the per cent. of the gas in the atmosphere. By means of a scale on the chimney the height is measured and the per cent. determined. In his experiments, Clowes obtained the following:

LIMITING EXPLOSIVE MIXTURES OF VARIOUS GASES WITH AIR.

Combustible gas used.	Percentage of gas in air. Lower explosive limit.	Percentage of gas in air. Higher explosive limit.	Method of kindling.
Methane	5	13	Upward
"	6	11	Downward
Coal-gas Nottingham	6	29	Upward
" "	9	22	Downward
Water-gas	9	55	Upward
Hydrogen	5	72	"
Carbon monoxide	13	75	"
Ethylene	4	22	"
Acetylene	3	82	Downward

The lower "limit" of inflammable gas represents the minimum proportion which, when mixed with air under ordinary conditions, will burn rapidly, and will, under certain conditions, produce explosions. If the proportion of inflammable gas mixed with the air is less than this in amount, the mixture will only burn in the immediate neighborhood of the kindling flame, and will not burn throughout. If, on the other hand, the proportion of inflammable gas in the air exceeds the maximum "limit" the gas will only be kindled and burn where it is in contact with an additional supply of air.

All proportions of gas intermediate between these limits are explosive when mixed with air, consequently the chance of an explosion resulting from the presence of one of these gases in the air is the greater, the more widely the "limits" are apart, since this gives rise to the possibility of a larger number of explosive mixtures being produced. Therefore the danger of explosion is least with methane and greatest with acetylene. Methane is a safer gas also because it has a high temperature of and a slow rate of ignition. All of these conditions tend to lessen the number of colliery explosions. It is to be noted that mixtures that cannot be ignited when the flame is applied to their upper surface may be fired from below, and this is the method of firing most likely to occur in coal mines. Few of the gases mentioned occur singly under conditions likely to give rise to danger. More commonly the combustible gases are present in a state of mixture as in water-gas and in coal-gas.

In giving "limits" it is assumed that the temperature of the mixture is not above 18° C. and that the pressure does not exceed seventy-six cm., for a gaseous mixture which is not inflammable under these conditions may become inflammable under increased temperature or pressure, and also that a mixture, that by ordinary test appears uninflammable, will propagate flame if a considerable volume of gas be projected into it, owing to the resulting increase in temperature and pressure. It will be observed that Clowes' detector reveals the presence of gas in proportions much below the danger-point, and gives timely warning.

The ignition of the fire-damp has been frequently caused by the gunpowder and "straw" used in blasting, for the outbursts of gas from the shaken coal and the outrush of flame and incandescent particles from the blast were often coincident. The use of electric primers and detonators remedied entirely the evils following the use of straws and naked fuse, and the employment of the high explosives gave greater immunity by reducing the frequency of the blasts. Greater security still has followed the use of the flameless explosives made from nitro-substitution compounds, or dynamites in which crystalline salts, like sodium carbonate and alum, containing a large amount of water of crystallization, are incorporated in the mass, or water cartridges, in which the explosive in the bore holes is placed in a water-bag or surrounded by moss, or other porous substances, saturated with water.

The occurrence of these mining accidents has caused the authorities grave concern and several of the European governments, notably Prussia, France, and England, have appointed many commissions, some temporary and others continuous, to investigate the reasons for the accidents and the methods of prevention. Many of the most prominent chemists of these countries have been called to serve upon the commissions and their reports have proved not only useful in the solution of the problem in hand but have been valuable contributions to chemical science. One of the more recent consequences of their deliberations is the establishment at Woolwich, England, of a station for testing all explosives offered for use in coal mines, and hereafter no explosives but those which successfully pass these tests can be used, and then only in the manner minutely described in governmental authorization.[1]

The closer study of the phenomena of explosions in gases, consequent on these investigations, has developed many interesting facts. Bunsen found that when mixtures of hydrogen and oxygen, and of carbon monoxide and oxygen in equivalent proportions were inflamed the union went on by fits and starts, and that the velocity of propagation of the reaction, through narrow orifices, was thirty-four meters per second in the hydrogen-oxygen mixture, and but one meter per second in the carbon monoxide-oxygen mixture.[2] Mallard tested various mixtures of methane and air, and coal-gas and air, in the same way finding the velocity of combustion to rapidly diminish as the proportion of inert gases present increased and obtaining a maximum speed in the case of eight volumes of air to one volume of marsh-gas of 0.56 meter per second.[3]

Berthelot using tubes of forty meters in length and five millimeters in diameter, obtained velocities of 2810 meters per second for hydrogen-oxygen, 1089 for carbon monoxide-oxygen and 2287 for methane-oxygen,[4] and found that the reaction could be propagated in three different ways. First, by combustion, as observed by Bunsen, in which the heat evolved is being continually lost through radiation and conduction, and in which consequently the pressure is exerted by the layer of burning molecules on their adjacent molecules and hence their velocity of translation tends constantly toward a minimum. Second, by detonation in which the heat evolved, the pressure produced by the reacting molecules on contiguous molecules, and the velocity of translation of the explosive reaction all tend toward the max-

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[1] Rep. Com. to inquire into the History of Explosives for Use in Coal Mines, Lond., 1897.

[2] *Ann. chim. phys.*, (4) 14, 449.

[3] *Ann. de Mines*, 8, (*1871*).

[4] Sur la force de la poudre, 1, 153.

imum. And finally, an intermediate stage all three being marked by distinct waves. Von Oettinger and von Gernet,[1] have by a very ingenious arrangement, succeeded in photographing first, a fundamental one which they style Berthelot's wave; second, more or less parallel secondary waves, whose existence they explain on Bunsen's hypothesis of the reflex action of waves due to successive explosions produced by the electric spark, and which they style Bunsen's waves; and third, polygonal waves of smaller amplitude. They obtained a velocity of 2800 meters per second which is of the same magnitude as those obtained by Berthelot.

Berthelot and Vieille's experiments show that when an explosion occurs in a gaseous mixture a number of ignited molecules are projected forward with a velocity corresponding with the maximum temperature produced by the chemical combination. The impact of these molecules causes the ignition of the adjacent particles, and the rate of progression of the combustion is thus dependent upon the activity of the chemical action.

Mallard and Le Châtelier find that the rate of propagation of flame through an inflammable gaseous mixture is affected not only by the temperature and size of the igniting flame, but also by the mechanical agitation or disturbance of the mixture itself. These results are not surprising when it is considered that for the spread of combustion in an inflammable gaseous mixture it is necessary that the temperature of the combustion should be sufficient to ignite the uninflamed portion.

Dr. W. H. Birchmore[2] has devised an apparatus for firing gaseous mixtures which shows many of these phenomena. He uses two large bulbs connected by a tube of determined dimension for his explosion chamber and a large tin-foil condenser for igniting the mixture, and he finds the phenomena to be different from those observed in tubes ignited in the ordinary way. The reaction takes place more promptly and sharply and when using hydrogen and air in variable amount not only is some of the oxygen ozonized but hydrogen dioxide is produced with the water of the reaction.

When using acetylene, with sufficient air to consume it theoretically, some of the carbon is separated out in the solid form

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[1] *Ann. der Phys.*

[2] *Am. Gas-Light J.*, 67, 563-565 (*1897*).

although free oxygen was found in the residues, and it was not until he had reached eight times the volume of air required by the theory that he got the theoretical amount of carbon dioxide.

He also describes a form of experiment which very cleverly illustrates the successive phenomena occurring in the acetylene explosion at Paris. The minimum volume of an inflammable gas which forms an explosive mixture with air is very considerably reduced if fine dust is present in the air. Buddle directed attention some ninety years ago in an account of the Wallsend Colliery explosion, to the destructive effect produced by the ignited coal dust at a distance from the point of first explosion. Robert Bald, in 1828, pointed out[1] that the blast of flame from a fire-damp explosion might ignite the coal dust on the floor of the pit. Faraday and Lyell, in their report on the Haswell Colliery explosion of September, 1844,[2] demonstrated that coal dust may be instrumental in greatly extending and in increasing the disastrous effects of fire-damp explosions. Abel[3] has shown that the presence of finely divided incombustible mineral matter in air containing less than two per cent. of fire-damp causes the latter to become explosive on ignition and Galloway has proved that a mixture of air containing less than one per cent. of fire-damp can be made to explode when charged with finely divided coal dust. I have applied this observation of the effect of the dust in facilitating explosions to lecture experiments with inflammable gaseous mixtures.[4]

The explosion at the Capitol on November 6th was confined to that portion of the building known as the supreme court section and which joins the senate wing to the central structure. In the center of this section is a dome which is rarely noticed as it is completely overshadowed by the central dome of the Capitol. This dome is supported in the subbasement on piers, while all about these piers are brick vaults and arches of varying heights, carrying the many partition walls and floors above them, and these, with those radiating from under the big dome and the connecting passages, form a perfect labyrinth. The complexity is increased by several of the spaces having been enclosed

[1] *Ed. Phil. J.*, 5, 101 (*1828*).

[2] Inst. C. E..Tracts, Vol. 284.

[3] Accidents in Mines, *Proc. Inst. Civ. Eng.*, (*1888*).

[4] *Proc. U. S. Nav. Inst.*, 12, 429 (*1886*).

with brick walls so as to carry steam-heating coils and for other purposes. A large part of the wall space had been fitted with shelving and these were filled to overflowing with pamphlets. One space was used as an engine room from which to operate a Sturtevant blower that fed air over the coils. This engine was provided with a woven guard screen to protect passers-by made from five-sixteenths inch wrought iron rods, riveted on each edge into two wrought iron bars each of which was seven-eighths inch wide by seven-sixteenths inch thick. Directly opposite this screen and leading south, was a low narrow passage that opened into one of the largest and highest of the vaults, in which was stowed, in the open spaces behind two supporting walls or piers, the ash from the wood fires which were burned in the rooms above. These hickory ash-pits, as they were styled, were south of and directly in line with the passage leading toward the iron screen. This series of compartments were on the extreme west of the subbasement. A few of the exterior compartments of the subbasement received a very little daylight but all the rest was wholly dependent on artificial light and several gas-jets were kept constantly lighted. In the center of the subbasement, under the dome, was a large gas-meter connected to a four-inch main and having on its outlet end a 200-light glycerine gas-governor. This meter had not been in use for some time and the inlet valve was closed but the outlet valve was open and it was discovered afterwards that this outlet pipe was also connected with a live four-inch main. The explosion occurred about 5.15 P.M. and its effects were observed over 47,000 cubic feet of the basement and upward quite to the dome. By the explosion the brick arches, covered with earth and then with heavy stone pavement slabs were torn up, brick partition and supporting walls were overthrown, stout locked doors on the upper floors were torn open and there was a general wrecking of all the lighter structural parts. Observation of the lay of the wreckage showed conclusively that it radiated in all directions from a point about the gas-meter and that the most violent effects were in general at the points most distant from this center. The most violent effect of all was on the west where the heavy granite screen wall, forming the façade of the building, was displaced by one and one-half inches and the stout wire protecting screen about the engine was forced in to a depth of two feet from the original plane for an area of three feet in diameter and many of the stout rods were ruptured. Searching examination showed that no explosive or other explosive-forming material than illuminating gas could have been present; that for thirty minutes prior to the explosion there was for some reason a gas pressure of twice the normal; that, under an excessive pressure, gas would flow through the governor; and that this could furnish sufficient gas to do the work accomplished.

The gas had a specific gravity of 0.601 and as it escaped it flowed through the devious passages and compartments filling first the pockets with mixtures of various proportions and settling lower and lower until the stratum reached down to the level of the burning gas-jets where it was fired. These were near the meter where of course the gas would be richest. Here was the region of combustion. As the tongue of flame rushed under the low archways and through the passageways to the higher vaults beyond it produced a violent disturbance of the atmosphere, thoroughly commingling the gas and air and throwing a mass of inflamed gas into their midst thus producing a greatly accelerated combustion and explosion. When this tongue of flame burst into the compartment containing the hickory ash this dust was also intimately commingled with the gas-laden atmosphere and here was produced the most violent of all the effects manifested; for the granite screen wall that was displaced was on the right side of the hickory ash-pits and the stout wire screen that was perforated was directly in front of them and at the end of the low and narrow passage leading from the vault containing these pits; and further the most violent effects produced on the upper floors, quite to the top of the building, were about the spiral staircase, leading from the compartment containing the wire screen and which was but a continuation, through the low narrow passage, of the compartment containing the hickory ash.

[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, NO. 4.]

PREPARATION OF METALLIC TELLURIUM.[1]

BY VICTOR LENHER.

Received January 20, 1899.

JUST a year ago a study was begun on tellurium. The material at hand on which the research was to be made consisted of the so-called electrolytic copper slimes furnished by the Baltimore Electric Refining Company. The first step was naturally to extract the tellurium from these residues, then to work up the metal obtained into such derivatives as might be found convenient for study. The first method employed consisted in the treatment of the residues with concentrated hydrochloric acid; chlorides of the soluble elements were formed, while a highly siliceous residue remained insoluble. The resulting solution was poured into water, when the oxide of tellurium was precipitated along with more or less antimony oxychloride. This precipitate was again dissolved in hydrochloric acid and sulphur dioxide conducted into the solution when tellurium was precipitated in a finely divided condition.

A process similar to the above is at present the general way by which the metal is obtained. The German tellurium which is on the market is obtained by treatment of the ore with aqua regia and the subsequent precipitation from a hydrochloric acid solution by sulphur dioxide.

A number of methods for obtaining metal are known, but most depend on the precipitation of the tellurium from a hydrochloric acid solution by sulphur dioxide.

Berzelius fused the naturally occurring tellurides with a mixture of oil and soda or potash, or with potassium tartrate. He obtained purple potassium telluride, which, subjected to the moderate oxidation of a current of air yielded tellurium according to the equation:

$$K_2Te + O + H_2O = 2KOH + Te.$$

Berthier treats nagyagite, which is a combination of gold telluride and lead sulphide with hydrochloric acid; hydrogen

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[1] Read at the New York meeting of the American Chemical Society, December 27, 1898.

sulphide is evolved, lead, antimony, etc., pass into solution, while the gold telluride is unattacked. The latter is treated with nitric acid, which dissolves the tellurium away from the gold. The tellurium is brought into hydrochloric acid solution by evaporation with hydrochloric acid and the tellurium precipitated by sulphur dioxide. Petzite is fused with a mixture of sodium carbonate and potassium nitrate. He extracts the tellurate with water, treats with hydrochloric acid to reduce to tellurite, after which he precipitates with iron. Berzelius extracts in a similar manner, but reduces his tellurate to telluride by fusion with carbon.

Schroetter treats tellurides with either hot concentrated sulphuric acid or aqua regia. The gold is precipitated with ferrous sulphate or oxalic acid and the tellurium by zinc. He reprecipitates the tellurium from a hydrochloric acid solution by sulphur dioxide or an alkaline sulphite. Another method of extraction is to treat the ore with chlorine gas, when tellurium chloride is formed and distils from the non-volatile portion. The tellurium is subsequently precipitated from hydrochloric acid solution by sulphur dioxide. The method doubtless owes its origin to Berzelius. It has also been suggested to prepare tellurium by precipitation with the electric current.

In 1870 Stolba called attention to the precipitation of tellurium from its alkaline solutions by means of grape sugar; later, Kastner found that it was completely precipitated by grape or invert sugar. But after those two papers the sugar precipitation has been very little heard of; it seemed as though it should be an ideal means of producing metal from the electrolytic copper residues as the tellurium appears as a waste product and is already in alkaline solution.

A series of experiments was made to attempt the extraction of tellurium by different methods. The first thing to do was to prepare tellurium by a well-known method and obtain a product that it would be possible to use in comparison. To this end, five pounds of residues were treated with concentrated hydrochloric acid (sp. gr. 1.20). An amber-yellow liquid was obtained and a residue which was highly siliceous. It is possible to obtain a perfectly clear solution by filtration through asbestos wool, using a suction-pump. When sulphur dioxide is brought into contact with such a strong acid solution, selenium should be precipitated free from tellurium according to Keller.[1] When sulphur dioxide was introduced into this solution a red precipitate formed showing selenium was just precipitated. It appeared to darken, however, when the liquid was saturated. On boiling, the precipitate agglomerated into a mass which much resembled selenium, but on separating it by means of potassium cyanide, it was found to consist of 3.2 grams of selenium and 28.3 grams of tellurium. This seems to indicate that tellurium and selenium cannot be perfectly separated by sulphur dioxide in strong hydrochloric acid solution. The filtrate from the strongly acid solution was diluted with water and more sulphur dioxide passed through the liquid, when the rest of the tellurium was precipitated. The lump of metal which was formed by fusion was finely powdered and fused with potassium cyanide; purple telluride of potassium was formed. The solution was filtered and a current of air passed through. The tellurium which was formed was fused, then distilled in hydrogen gas. This material was considered pure. When treated with aqua regia, dioxide is formed and may be obtained by evaporation. Tellurium oxide is completely volatile at a low temperature in hydrochloric acid gas, no residue remaining. Pure tellurium is likewise completely volatile when heated in hydrogen.

Since it seems most natural to prepare a metal from its oxide, the tellurium oxide was subjected to a number of reduction tests. In recent years, metallic magnesium and metallic aluminum have shown themselves to be of great value as reducing agents. When metallic aluminum and tellurium oxide are heated together in a crucible a violent reaction takes place; tellurium is formed, but immediately unites with the aluminum forming aluminum telluride. Metallic magnesium, even in very coarse condition, when heated with tellurium oxide, gives a very explosive reaction. So very energetic is the action that it has not been possible to collect any of the products formed.

When dry glucose is heated with the oxide, a coke is formed which becomes coated with the metal and is difficult to fuse into a button. The same may be said of a dry fusion of asphaltum

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[1] This Journal, 19, 773.

with the oxide. Ignition of the oxide with dry oxalic acid does, however, give metal readily, and fusion into a globule is an easy matter.

The next series of experiments was made with the sugars. Tellurium oxide was dissolved in potassium hydrate, cane-sugar was added, and the solution warmed. When a saturated solution is used, purple telluride is formed, but boiling in contact with the air causes a rapid separation of black tellurium. After washing with water the precipitate can be dried and fused into a mass.

From a solution of an alkaline tellurite glucose precipitates black elementary tellurium. No intermediate formation of telluride could be noticed as with cane-sugar. Pure white, anhydrous grape-sugar was dissolved in water and added to a warm solution of the alkaline tellurite. Tellurium was precipitated in elementary form. During the process of washing, which always followed the precipitation, it was invariably noticed that grape-sugar was much more difficult to remove from the finely divided tellurium than any of the other sugars.

From these experiments it seemed natural to conclude that reducing sugars will give a very practical method for the preparation of metallic tellurium. Tellurium obtained by this method is completely volatile in hydrogen gas and its oxide is likewise volatile in hydrochloric acid gas.

Thanks to the kindness of Mr. Walker, of the Baltimore Electric Refining Company, who furnished the residues, and to Prof. P. de P. Ricketts, who in so many ways made the work possible, the author has been enabled to prepare a bar[1] of tellurium by fusion of the finely divided material obtained by reduction of tellurium in alkaline solution by means of sugar.

Among other experiments, I decided last year, while working on selenium, that as soon as I could obtain satisfactory compounds I should determine the atomic mass of tellurium by precipitation with hydroxylamine. As my work thus far on tellurium, which was begun with Prof. E. F. Smith at the University of Pennsylvania, and is now going on in this institution, had for one of its objects the determination of the atomic mass

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[1] This bar was exhibited before the American Chemical Society, at New York, and weighed four pounds.

of tellurium by means of the hydroxylamine precipitation it seems quite proper that I should continue it, notwithstanding the fact that Prof. Jannasch, of the University of Heidelberg, announced in the *Berichte* for October, 1898, that he is engaged in work on the same line.

THE ASSAY OF NUX VOMICA.[1]

BY EDWARD R. SQUIBB.

Received December 30, 1898.

IN the preparation of a paper on acetic acid as a substitute for ethyl alcohol in extracting the active principles of some officinal drugs, it became necessary to have a convenient and moderately accurate method of assaying nux vomica. The whole of this paper would interest very few members of the American Chemical Society, and such as it would interest may find it in the *American Journal of Pharmacy* for January, 1899. But the assay process that ends the paper may be far enough within the line of interest to this society to warrant the writer in offering it here.

The short and easy methods of Messrs. Dunstan and Short, given in the *British Pharm. Journ. and Trans.*, 3d Series, 13, 665–1055, and 14, 621, and given in the British Pharmacopœia, were found objectionable on some accounts, but chiefly because the results are too high. For example, a table is given on p. 1055, wherein from seven samples the percentage of total alkaloids ranged from 3.04 to 3.90 per cent. with an average of 3.29 per cent. This, in the writer's experience, is much too high, and there is a probability that the plus error may be due to weighing the chloroform extract as alkaloid. The most recent authority noticed is the new, 1898, British Pharmacopœia, but its method is liable to the same objection of weighing a chloroform extract as alkaloid. The U. S. Pharmacopœia of 1890 has an excellent method that avoids this source of error by titrating the alkaloids. This method[2] first makes a dry extract and then assays that for use in its standardized preparations.

Two grams of the dry extract are dissolved by shaking in a separator with twenty cc. of a previously-made mixture of two

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[1] Read at the New York meeting of the American Chemical Society, December 28, 1898.

[2] U. S. Pharmacopœia (*1890*), pp. 152 *et seq.*

volumes of alcohol (ninety-one per cent.), one volume of ammonium hydroxide (ten per cent.), and one volume of water. Then twenty cc. of chloroform (ninety-nine per cent.) is added and the mixture is agitated during five minutes. The chloroform is then allowed to separate and is drawn off as far as possible by the stop-cock. This washing out is repeated with two further portions of chloroform of fifteen cc. each. The chloroform solutions are then collected in a beaker and exposed on a water-bath until the chloroform and ammonia are completely dissipated.

Then ten cc. of decinormal sulphuric acid is added, stirred, diluted with twenty cc. of hot water, and when solution is complete two cc. of brazilwood indicator is added. Centinormal potassium hydroxide is added until a permanent pinkish color is produced. The number of cubic centimeters of potassium hydroxide required is divided by 10, the number found is subtracted from 10, and the remainder is multiplied by 0.0364, and that product by 50, which will give the percentage of total alkaloids in the two grams of extract taken, it being assumed that strychnine and brucine are present in equal proportion, and the above factor being found by taking the mean of their respective molecular weights ($334 + 394 \div 2 = 364$).

This very well-designed method was found impracticable in the writer's hands, through difficulty in carrying out the details. The first obstruction encountered was the very nearly constant emulsifying of the chloroform and the consequent refusal of the liquids to separate on standing, and the difficulty and loss of time in managing an emulsion once formed. The U. S. Pharmacopœia directs the immiscible liquids to be "agitated," not shaken; yet if shaking be avoided and the agitation be ever so cautiously managed, some emulsion seems unavoidable, whilst a degree and kind of agitation that is short of shaking washes out the alkaloids imperfectly. Emulsions that did form were best managed by running them out into a capsule, driving off the chloroform on a water-bath, returning the dark liquid to the separator, and managing the next chloroform with greater care. But a better expedient was found in a recommendation of A. H. Allen and others, to use a mixture of equal volumes of chloroform (ninety-nine per cent.) and ether (ninety-six per cent.(. With this mixture, used in large quantity, vigorous shaking and consequent effective washing may be employed with little emulsion, if any, at the last of the washings, the separations being very prompt and sharp, usually ready to draw off within half an hour after shaking. The clear chloroform and ether solutions are better managed if drawn off into and boiled off from a flask, as the dissolving, the heating up, and the titration are more easily done in a flask. The solution to be titrated is always of a full yellow color, from a bright pale yellow to a deep yellow, with a reddish tint by reflected light; a color in which the first increase of pinkish tint is difficult to detect, and the want of sharpness and decision in this end-reaction is the persisting difficulty with all methods of titration that were tried, but in comparing indicators brazilwood was found to be inferior to logwood. A decinormal potassium hydroxide is preferable to centinormal, as it does not dilute the solution of alkaloids so much, while in accuracy of reading it is far within the limit of error of the indicator.

Chiefly in consideration of these conditions the following method was reached and used:

A fair sample of nux vomica is drawn and an average dozen or so of the seed is so milled as to pass through a No. 9 sieve. Of this ten grams are weighed off and exhausted with ten per cent. acetic acid. This exhaustion is easily and conveniently done in a Soxhlet apparatus, but so large an amount of extractive is washed out by the warm acid, that the extract is very difficult to dry, and afterwards at once forms an emulsion that is difficult and tedious to manage. Cold percolation to complete exhaustion gives a much better result, and is not difficult to effect, provided the powder be moistened for packing with not more than ten cc. of the acetic acid, and be not packed too tightly.

The percolate is evaporated to dryness on a water-bath, in a large (twelve cm.) flat-bottomed capsule, so that the extract is in a thin layer, easy to dry and easy to dissolve. The weight gives the yield of extract.

If a fluid extract or tincture is to be assayed, it is measured, weighed, and dried in the same way.

A mixture is made of two volumes of alcohol (ninety-one per cent.), one volume of ammonium hydroxide (ten per cent.), and one volume of water, and of this, ten cc. are poured upon the dry extract in the capsule. Then by patiently moving a stirrer over the smooth surface of the dry extract for a quarter of an hour or more, a smooth solution of the extract, easy to wash, is obtained. This is poured into a separator of 150 cc. capacity, and the capsule and stirrer are rinsed clean with ten cc. more of the alcohol and ammonia solution.

A mixture is made of equal volumes of chloroform (ninety-nine per cent.) and ether (ninety-six per cent.), and forty cc. of this is added to the liquid in the separator; the whole is shaken vigorously during five minutes, and then allowed to separate. In twenty to thirty minutes the separation will be complete to a sharp line, when the depth of the upper, dark stratum should be observed and measured. The chloroform-ether solution is then drawn off into a tared flask of about 100 cc. capacity, and the flask is immersed in a hot water-bath so that the chloroform-ether may be boiled off by the time another washing is ready. In the meantime forty cc. more of chloroform-ether have been added to the contents of the separator, and the shaking, separating, and drawing off into the flask repeated. This second washing may or may not be then followed by a third, managed in the same way, if required.

If after standing, to separate completely a second time, the dark liquid on top shall be found to have increased in depth, the indication is that emulsion has been formed to that extent, and that the chloroform forming that emulsion holds the proportion of alkaloids present in solution at the time that emulsion was formed, and as the chloroform cannot be washed out of an emulsion, so the alkaloids held by that chloroform cannot be washed out. Therefore, in the case of any considerable amount of emulsion after the chloroform-ether solution is drawn off into the flask, the dark liquid is drawn off into the flat capsule and warmed on a water-bath until all the chloroform-ether is driven off. The dark liquid is then returned to the separator and again washed as before. If a small amount of emulsion again forms, as very rarely occurs, the chloroform in it holds so very little alkaloid as to be within the limit of error of the method.

The tared flask will then contain the total chloroform extract, and the weight of this was long erroneously accepted as the weight of alkaloids.

Ten cc. of decinormal sulphuric acid are now carefully measured from a burette into the flask, which is rinsed round and warmed by immersion in a water-bath until the soluble alkaloids are dissolved, when the insoluble residue will show how much of this extract is not alkaloid.

Twenty cc. of hot water are added to the contents of the flask, and a definite quantity (ten drops) of logwood indicator. The color is then closely observed by transmitted light, and matched by a similar quantity of liquid in a similar flask. Decinormal potassium hydroxide is now dropped in from a burette until the color changes slightly to a pinkish tint or shade of the original yellow by transmitted light, and when this hardly perceptible change is now looked at by reflected light the pink tint is very distinct.

The number of cubic centimeters required subtracted from 10 (cubic centimeters of acid used) gives the number of cubic centimeters of acid saturated by alkaloids, and this number multiplied by the mean of the molecular weights of the two alkaloids ($0.0334 + 0.0394 \div 2 = 0.0364$), gives the amount of alkaloids obtained from ten grams of nux vomica, the strychnine and brucine being assumed to be present in equal proportions.

Then as 10 is to the product from 10, so is 100 to the percentage of the mixed alkaloids.

DETECTION OF CARAMEL IN SPIRITS AND VINEGAR.

BY C. A. CRAMPTON AND F. D. SIMONS.

Received February 13, 1899.

HAVING had frequent occasion to determine the question as to whether a sample of spirits was colored with artificial coloring-matter or owed its color to a long age in wooden packages, one of us has for a long time endeavored to obtain some reliable test by which the presence of caramel could be definitely proved. The principal methods given in the books are (1) the reducing action of caramel on Fehling's solution, and (2) the precipitation of the coloring-matter by paraldehyde. Neither of these methods has given satisfactory results in our hands. Spirits extract from oak wood, especially when charred, substances which have nearly, if not quite, as high a reducing power on Fehling's solution as caramel. The test with paraldehyde, known as Amthor's test,[1] is given greater weight in most text-books, and is mentioned by Smith[2] in a recent article on vinegar analysis. This test has proved equally as unsatisfactory in our hands as the reduction of copper. When present in large quantities the caramel may possibly be obtained as a precipitate and identified by its action on phenylhydrazine, but in the small amount present in artificially colored spirits, for example, the precipitation is imperceptible.

In searching for a more reliable test, our attention was drawn to the action of fuller's earth upon coloring-matters, and especially to the article by Geisler,[3] showing the effect of fuller's earth upon the artificial azo-dyes used in butter or oleomargarine.

Upon adding this earth to samples of spirits colored in the natural way by contact with charred or uncharred wooden packages, we found the color but slightly affected, while using the same quantity upon spirits colored artificially with caramel, a very large part of the color was discharged. In other words, the earth seemed to have a much stronger affinity for the artificial than for the natural coloring-matter. By means of Lovibond's tintometer the difference in color before and after the treatment may be determined with a considerable degree of accuracy, and in this way more than twice as much color was found to have been absorbed from artificially colored spirits as from the natural.

The test was applied to all the samples of both kinds which were available, some fifty-eight in number, and no exceptions found. A series of forty samples of spirits known to be naturally colored gave the following figures:

	Color removed. Per cent.
Maximum	25.0
Minimum	8.3
Average	14.6

A series of eighteen samples of spirits known to be artificially colored gave the following figures:

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[1] Koenig: *Nahrungs- und Genussmittel*, Band II, p. 1026.

[2] This Journal, 20, 3 (*1898*).

[3] *Ibid.*, 20, 110 (*1898*).

	Color removed. Per cent.
Maximum	54.1
Minimum	40.0
Average	44.7

It will be seen that the margin is ample for detecting a sample colored artificially ; the average per cent. of color removed from the factitious samples being about three times as great as the average per cent. removed from the genuine samples, while the maximum and minimum of the two sets are fifteen points apart. It must be remembered that all the artificially colored samples have, besides the added color, a small amount of natural color derived from wood, and this varies in different samples. If this were not the case, a much greater disproportion would be shown between the results before and after the treatment. A sample of water-white spirits which we colored ourselves with caramel, and then subjected it to the usual treatment, lost seventy per cent. of its color.

The test must be made strictly comparative, of course, the same amount of the absorbent material being used in each case, and allowed to remain in contact with the liquid a certain length of time at normal temperatures. A sample of spirits colored naturally may be used as a standard which should not be too far removed from the suspected sample or samples in depth of color, though if a colorimeter be used it is not at all necessary for the standard to be the same depth of color as the suspected sample. The method of procedure followed in our work was as follows: Twenty-five grams of fuller's earth was added to fifty cc. of the spirits under examination, the mixture beaten up in a beaker, allowed to stand covered half an hour at room temperature, and filtered. The determination of the figure representing the color was made with the tintometer upon the liquid before and after treatment, and the difference between the two results gave the percentage of color absorbed. It is scarcely necessary to say that the same earth must be used in all cases. We have only been able as yet to examine two different samples of this material, and these differed considerably in their power of absorbing the caramel coloring. It is known that some varieties of fuller's earth do not have the property of absorbing color at all.

The test was also applied to two samples of cider vinegar known to be pure, that is, with no artificial coloring-matter added, and the result showed that but a slight effect was produced upon this coloring-matter by the earth. Caramel was then added to these samples and they were again treated with the earth, with the result that the added coloring-matter was almost entirely removed and the samples restored to practically their original color. Acetic acid diluted to vinegar strength and colored with caramel gave up its color when treated. These few experiments seem to show that the test is applicable to vinegar, but we have not had the facilities for extending it to a large number of factitious samples as we have done in the case of spirits.

The color-absorbing power of fuller's earth is a most interesting subject, which does not appear to have been investigated to any extent. Whether it is due to chemical or physical action, and the connection, if any, between the composition of the earth (which seems to be anything but uniform) and its effect upon various coloring-matters, are questions which should receive attention and would doubtless yield interesting and valuable results to investigation. If any work has been done along this line no results have been published, as the journals make little or no mention even of the fact that fuller's earth possesses such properties. Yet it is well-known that a very extensive industrial use has been made of it within recent years in the refining of both vegetable and mineral oils. We have been informed that filtration through or treatment with fuller's earth has entirely superseded all other methods of bleaching in the cottonseed oil industry. Our results showing its affinity for caramel coloring would seem to indicate that it might be substituted for bone-black in sugar clarification, but we are not aware that such application has been made. Perhaps it would be considered too much like a return to the ancient method of "claying" sugars.

A STUDY OF THE RELATIVE VALUE OF LACMOID, PHENACETOLIN AND ERYTHROSINE AS INDICATORS IN THE DETERMINATION OF THE ALKALINITY OF WATER BY HEHNER'S METHOD.

BY JOSEPH W. ELLMS.

Received January 12, 1899.

IN the determination of the alkalinity of water for sanitary and technical purposes, Hehner's method offers theoretically as scientific and accurate a process as could be desired. The accuracy of the method as it is usually carried out is lessened, however, by the character of the indicators which one is obliged to employ. The color changes of these indicators are unfortunately rather indistinct and therefore introduce into the determination the personal equation of the operator.

The titration with sulphuric acid of the calcium and magnesium carbonates dissolved in water, as this method directs, necessitates the use of indicators which either are not susceptible to the carbonic acid liberated in the reaction, or to its removal as soon as formed, when using indicators which are sensitive to this acid.

Quite a number of indicators have been advocated by different writers and for the most part they fail to agree as to the one best suited for this determination. Hehner[1] in his original notes upon the method recommends the use of phenacetolin. Thomson[2] prefers lacmoid and considers phenacetolin indistinct in its color changes, requiring too much skill for its successful use by the ordinary analyst. Draper[3] considers either lacmoid or carminic acid as well suited for this determination, but favors the latter indicator as being somewhat less susceptible to carbonic acid. Methyl orange has also been employed by some analysts with considerable success.

Erythrosine[4] was first proposed as an indicator by Mylius[5] and Foerster, but the writer is not aware that it has ever been com-

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[1] *Analyst*, 8, 77.

[2] *Chem. News*, 47, 123, 185.

[3] *Ibid.*, 51, 206.

[4] Sutton's Volumetric Analysis, §14, p. 39.

[5] *Ber. d. chem. Ges.*, 24, 1482; also *Chem. News*, 64, 228.

monly used for this determination, and as its use requires a somewhat different procedure from that employed with the ordinary indicator, it will be described in detail beyond.

Having occasion to employ Hehner's method for a long series of alkalinity determinations, a number of experiments were undertaken with a view to determine the relative value of the three indicators, lacmoid, phenacetolin, and erythrosine, and if possible to fix definitely upon the color change which corresponded with the completion of the reaction. Considerable attention was paid to the technique of the titration, and especially to the improvement of the original method of Mylius and Foerster when erythrosine was employed as an indicator. A detailed description of the process as carried out with the several indicators may therefore be of interest.

SOURCE, COMPOSITION, AND PREPARATION OF THE THREE INDICATORS.

Lacmoid and phenacetolin, as described by Sutton and other writers, are prepared as follows:

Lacmoid is derived from resorcin by heating with sodium nitrite at a temperature of 110° to 120°C., dissolving the product in aqueous ammonia and reprecipitating with hydrochloric acid. It is then washed free from acid and dried. The varying shades of color of the alcoholic solution of different samples of this substance are probably due to the thoroughness with which the last traces of acid are removed. For titration work a solution is prepared by dissolving two grams of the substance in one liter of fifty per cent. alcohol.

Phenacetolin is prepared by boiling together for several hours phenol, acetic anhydride, and sulphuric acid. The resulting product is washed with water to free from acid, and dried. Two grams of the substance are dissolved in one liter of strong alcohol for use as an indicator.

Erythrosine or iodeosine is a product of resorcin-phthalein or fluorescein. The halogen substitution-products of the latter form a series of fluorescing dyes among which is the well-known dye eosine. Eosine, the potassium salt of tetra-bromo-fluorescein ($C_{20}H_6Br_4O_5K_2$), has its counterpart in the iodine substitution-compound tetra-iodo-fluorescein or erythrosine ($C_{20}H_8I_4O_5$).

Mylius and Foerster, who made an extended study of this substance, describe the commercial product, which is used in cotton printing and paper staining, as a brick-red powder soluble without fluorescence, but with a rose color in dilute alkalies. The above investigators purified their product for the purposes of their experiments, but the sample of dye used in this work showed no impurities which in any way interfered with the experiments undertaken and it was therefore used just as it was obtained on the market.

The sample employed in the writer's experiments was apparently the sodium salt of erythrosine. It was practically insoluble in ether and chloroform, but soluble in water with a slight fluorescence, the latter property increasing with the dilution, and slightly soluble in aqueous ether. An aqueous solution of erythrosine containing one-tenth gram in one liter of water is prepared for use as an indicator.

TECHNIQUE OF THE DETERMINATION WITH THE SEVERAL INDICATORS.

Lacmoid.—One hundred cc. of the solution to be tested are introduced into a six-inch porcelain evaporating dish, and placed on a stand over a free flame. The liquid is heated until bubbles begin to break at the surface and then the dish is quickly removed. The temperature of the water when titration commences should be about 75° C. One-half cc. of the indicator solution is next added and then sulphuric acid (fiftieth-normal) until the solution shows no change in color as a drop of the acid strikes the surface of the liquid and sinks to the bottom of the dish. After the addition of the acid drop by drop toward the end of the titration, careful stirring should follow as the diffusion does not appear to be very rapid. This gives a uniform reddish or purple color to the liquid which becomes more marked immediately under and around the acid as it sinks into the water.

Phenacetolin.—The preliminary portion of the operation with this indicator is the same as for lacmoid. One-half cc. of the indicator is added and the titration carried on as the preceding one until no change in color occurs immediately about a single drop of the acid as it strikes the surface of the liquid and sinks to the bottom of the dish.

Erythrosine.—Mylius and Foerster in their study of erythrosine prepared an aqueous ether solution of iodeosine for their indicator solution. This indicator when shaken with the alkaline solution to be tested imparts a rose color to the latter. A slight excess of acid, upon neutralization of the alkali, discharges the rose color, leaving the aqueous solution colorless.

The disadvantages arising from this ethereal solution led the writer, after considerable experimenting, to abandon its use and in its place was substituted an aqueous solution of the erythrosine. Beside this, chloroform was employed in the titration, the latter acting in a manner similar to the aqueous ether. As a result of this experimental work the following modified process was devised.

The titration is made in a vessel which can be shaken and preferably in a 250 cc. white-glass flat-stoppered bottle. One hundred cc. of the water are placed in the bottle with two and five-tenths cc. of the aqueous solution of the erythrosine and five cc. of chloroform. They are well shaken together and the acid added in small quantities, followed each time by a thorough shaking of the bottle. The rose color of the water toward the end of the titration becomes less marked and upon the addition of a very slight excess of acid the color disappears completely The chloroform disseminated through the liquid produces a milky appearance on account of the frequent shaking; but this is no especial hindrance to determining the end-point, although one can wait until the chloroform[1] settles to the bottom of the bottle if desired. A white paper held at the back of the bottle facilitates the detection of any trace of color remaining as the titration approaches the end-point.

For the calculation of results the value of the approximate fiftieth-normal sulphuric acid, standardized against a fiftieth-normal sodium carbonate solution, is first determined and the amount of acid used up by the water tested is expressed in terms of calcium carbonate. In accurate work it is advisable for reasons which will be pointed out later, to employ a correction for the indicator. This may be done by using a measured volume of the indicator and determining the amount of acid required to effect the color change in a blank determination with distilled

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[1] The chloroform residues may be saved, washed with dilute potassium hydroxide solution and then with water. The chloroform may then be distilled and used again.

water. The volume of acid thus found is deducted from all readings before converting them into terms of calcium carbonate.

THEORY OF THE ACTION OF THE SEVERAL INDICATORS AND A DISCUSSION OF THE END-POINTS.

The action of the different indicators briefly considered from the standpoint of the present theory of solution will perhaps bring out the reason for certain difficulties connected with their use.

Lacmoid and phenacetolin are moderately acid indicators which are intermediate between methyl orange, a rather strongly acid indicator, and phenolphthalein, a weakly acid indicator. In the presence of the alkaline carbonates of lime and magnesia, the ionized lime and magnesia salts of the indicator used are first formed. Upon adding a strong acid like sulphuric, a fairly sharp color change is obtained when the carbonates present have become neutralized. This color change is the result of the action of the free hydrogen ions, in the slight excess of acid added, upon the dissociated salt of the indicator. The change from one color to another is coincident with the conversion of the dissociated salt of the indicator, with the color due to its free complex ion, to the acid form of the indicator, having in its non-ionized or acid form another color or as in the case of phenolphthalein, none at all.

The reason for the indistinct color changes in the case of lacmoid and phenacetolin is that the non-ionized molecules of both these indicators are colored themselves, in the case of lacmoid a red or purple and in that of phenacetolin a yellow. The ionized salts are blue and pink respectively. The passage of the blue to the purple in the case of lacmoid and the pink to the yellow in the case of phenacetolin, is somewhat confusing to the eye on account of the mingling and blending of the colors. In this way the end-point is rendered less sharp than it would be if the non-ionized molecules of the two indicators were colorless as in the case of phenolphthalein. Like methyl orange they are more or less dissociated in solution, even in the absence of bases and the colors of the complex ions become apparent. For this reason the amount of indicator added in the titration, especially in using dilute acid solutions, should be carefully controlled, and in very accurate work measured. The amount of acid necessary to bring about the requisite color change can then be carefully determined in a blank experiment.

Another difficulty which arises in the use of lacmoid and phenacetolin is their susceptibility to carbonic acid. As this is formed in the course of the reaction between the sulphuric acid and the carbonates of the bases present, it must be removed by heating the solution. While carbonic acid is one of the very weak acids, yet its acid character is appreciably greater than that of the indicators in question and therefore interferes with the true end-point, unless it is practically all eliminated from the solution as soon as formed.

To consider the end-points with lacmoid and phenacetolin from a practical point of view in titrating for carbonates in water, the question may very properly be asked, When is the neutralization of the carbonates complete? It seems to the writer that the unsatisfactory results obtained with this process are largely due to a lack of knowledge of the true end-point. Obviously the only means of fixing this point is by working with known solutions of sodium, calcium, and magnesium carbonates and checking them against each other.

As has been stated in a preceding paragraph the true end-point determined by working with known solutions is, in the case of lacmoid, the point where no change in color can be detected as a drop of the acid enters the liquid. The change in the color of the whole liquid should properly have ceased to be appreciable for three or four drops, possibly, preceding the true end-point, but if very carefully watched a drop of the acid, as it enters and sinks to the bottom of the dish, will produce about it a brighter reddish or purple color than that of the surrounding liquid. When this phenomenon can no longer be detected the titration is complete.

The same conditions hold true for phenacetolin, and the golden color produced about a drop of the acid as it sinks to the bottom of the dish should be evidence of the incompleteness of the titration and acid should continue to be added until this color change is no longer produced. These end-points require care and skill and some practice in order to be recognized, but these are difficulties which are not so serious as to bar the use of these indicators in accurate work.

Erythrosine on account of the peculiar manner in which it is used demands a somewhat different explanation of its action. Mylius and Foester state the following facts regarding erythrosine, many of which have been confirmed by my own experiments:

Iodeosine is soluble to a slight degree in water with some rose color, the same as with its solution in alkalies. The red color, of an aqueous alkaline solution of the dye remains even after addition of quite an excess of acid, hence its unsuitability for use directly as an indicator. By adding a strong acid to an aqueous solution of the dye an orange yellow precipitate is formed called by them the 'anhydrous iodeosine'. The red color in solution, they state, is produced by formation of a hydrate, as in evidence they say the more water added to an alcohol or acetone solution, the redder the solution becomes.

The red solution of iodeosine hydrate in water may be decolorized by an excess of ether, although aqueous ether is more of a solvent for the hydrate than the water. Yet water will take up color when shaken with an ethereal solution of iodeosine.

Mylius and Foester evidently intended to explain the facts stated above by the theory of the formation of hydrates in solution, but they pointed out, however, that the phenomena could also be explained by the electrolytic theory of dissociation. It would seem a more plausible explanation of the phenomena to associate them with the latter theory and after a somewhat fuller explanation than that previously given of what takes place when using erythrosine as an indicator, the phenomena in question will be considered from that point of view.

The addition of the aqueous solution of erythrosine to a water, containing alkali in solution, intensifies the color quite a little. The deep rose color remains fairly bright until nearing the end of the titration when it fades away, becoming a rather faint orange. With a slight excess of acid, however, this disappears also. The chloroform, which at first was colorless, shows a brownish tint at the end of the titration and the water solution above appears colorless.

It would seem then that the chloroform, or ether as Mylius and

Foester used, is an essential part of the process, since without it no sharp end-point is possible. Erythrosine is evidently a rather strongly acid indicator from the fact that to an alkaline solution a large excess of acid must be added in order to form the non-ionized iodeosine molecule. In aqueous solution without the presence of alkaline bases it is also, to a certain extent, in the ionic condition, as shown by the red color of the solution due to the free complex ion. If, however, ether or chloroform are present, when using erythrosine as an indicator, the greater solubility of the substance in these solvents cause it to be dissolved out of the aqueous solution as soon as its non-ionized molecule is formed. When thus removed the neutralization of the alkali is immediately apparent and therefore a sharp end-point is obtained.

In an ether or chloroform solution the iodeosine is probably not dissociated at all and so only the color of its non-ionized molecule is apparent. In an alcohol solution an appreciable dissociation results which increases as the proportion of water to alcohol increases.

The phenomena stated by Mylius and Foester regarding the decolorization of aqueous iodeosine solutions with a large excess of ether and the imparting of color to water by ethereal solutions of iodeosine, can probably be explained by the laws relating to the extraction of a dissolved substance from one solvent by means of another, the solvents being non-miscible, and the extent of ionization and non-ionization of the substance in the two solvents.

The readiness with which the chloroform takes up the erythrosine in its non-ionized condition from the water, as soon as it is formed, is undoubtedly explained in a similar manner. The principle involved, it would seem, might be applied to other substances capable of acting as indicators and thus materially increase the number of compounds which could be used in this capacity. Carbonic acid under normal conditions has no appreciable effect on this indicator, thus placing it beside methyl orange in this respect, although in its chemical composition it differs very little from phenolphthalein, which is extremely sensitive to carbonic acid.

COMPARISON OF THE THREE INDICATORS IN TITRATION OF THE CARBONATES OF SODA, LIME, AND MAGNESIA.

In order to fix definitely upon the proper end-point when using lacmoid or phenacetolin as indicators and also to compare the results obtained with those when employing erythrosine, a series of titrations were made using known solutions of the carbonates of sodium, calcium, and magnesium. The solutions were prepared with considerable care and the amount of the salt dissolved determined gravimetrically. The titration work was carried on by two different observers. All the titrations were made in a volume of 100 cc. The amount of carbonate present was varied in the lime solutions, three dilutions being used, while with the soda and magnesia only one was employed.

The figures in the following table refer to the number of cubic centimeters of sulphuric acid required to neutralize five cc. of a fiftieth-normal sodium carbonate solution, after diluting to one hundred cc. with distilled water and titrating with the aid of the different indicators in the manner previously described.

STANDARDIZATION OF THE SULPHURIC ACID AGAINST A FIFTIETH-NORMAL SODIUM CARBONATE SOLUTION.

	Lacmoid.	Phenacetolin.	Erythrosine.
Mean of ten results	5.04	5.06	5.15
Maximum	5.20	5.10	5.20
Minimum	5.00	5.00	5.10
Percentage strength of acid in terms of fiftieth-normal sulphuric acid	99.1	98.8	97.0

The correction for each indicator, which has been deducted in the above table, is as follows:

One-half cc. of the lacmoid solution requires four-tenths cc. of the sulphuric acid to produce the end-point; five-tenths cc. of the phenacetolin solution requires 0.25 cc. of acid and two and five-tenths cc. of the erythrosine solution with five cc. of chloroform requires two-tenths cc. of acid.

SUMMARY OF RESULTS OBTAINED WITH KNOWN SOLUTIONS OF CALCIUM CARBONATE.

Group I.

Calcium carbonate.	Lacmoid.	Phenacetolin.	Erythrosine.
Parts present in solution[1]	67.8	67.8	67.8
Parts found, average of fifteen results	67.6	66.9	65.8
Percentage found of amount present	99.7	98.7	97.0

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[1] Amounts expressed in parts per million.

Group II.

	Lacmoid.	Phenacetolin.	Erythrosine.
Parts present in solution	40.7	40.7	40.7
Parts found, average of fifteen results	40.0	40.2	40.4
Percentage found of amount present	98.2	98.7	99.2

Group III.

	Lacmoid.	Phenacetolin.	Erythrosine.
Parts present in solution	27.1	27.1	27.1
Parts found, average of fifteen results	26.4	26.3	26.8
Percentage found of amount present	97.4	97.0	98.8
Percentage found, average of forty-five results	98.4	98.1	98.3
Maximum number of parts variation from amount present	3.0	3.0	1.5

SUMMARY OF RESULTS OBTAINED WITH A KNOWN SOLUTION OF MAGNESIUM CARBONATE.

Amount of $MgCO_3$ Present in all Titrations = 36.5 parts.

Magnesium carbonate.	Lacmoid.	Phenacetolin.	Erythrosine.
Parts found, average of five results	35.9	35.9	36.2
Percentage found of amount present	98.3	98.3	99.1
Maximum number of parts variation from amount present	1.0	1.0	0.5

From the preceding data it is quite apparent that any one of the indicators offers but little superiority over either of the other two. Erythrosine gives more uniform results and a larger percentage of the carbonates actually present with low amounts than with high amounts, while the reverse seems to be true of lacmoid and phenacetolin.

The only conclusion which can be drawn from the above data is that with a knowledge of the true end-point with lacmoid and phenacetolin and with proper care and skill all of the three indicators are suitable for Hehner's method, and that, if uniformity of results within very narrow limits is desired, the preference should be given to erythrosine. The average error of determination when employing any one of these three indicators ought not in good work to exceed ± 1.5 per cent.

Thomson has very fully described the bases capable of being determined with lacmoid and phenacetolin and the salts interfering with their action. Mylius and Foester made use of erythrosine for the study of the neutrality of salts, and certain facts which they brought out are of interest in connection with this determination.

The alkalies, alkaline earths, salts of cadmium, manganese, nickel, and cobalt are alkaline to erythrosine. The oxygen salts of iron, aluminum, and chromium behave like free acids to this indicator. It is not suitable for the titration of organic acids; and even oxalic acid cannot be used. Ammonia, however, may be titrated with it. Erythrosine may be used with fairly turbid waters and also with colored waters. In this respect it is much better than lacmoid or phenacetolin, both of which tend to give too high results with such waters.

LABORATORY OF "COMMISSIONERS OF WATER WORKS,"
CINCINNATI, OHIO, January 10, 1899.

SOME NOTES ON THE ESTIMATION OF CARBOHYDRATES.

BY F. W. TRAPHAGEN AND W. M. COBLEIGH.

Received December 20, 1898.

IN common with agricultural chemists in many parts of the country we have been interested in the direct determination of the carbohydrates of grains, foods, etc., in place of the method of subtracting from one hundred all other constituents and calling the remainder "nitrogen-free extract."

It seemed to us, as it was necessary to take advantage of the cupric reducing power for the estimation of the carbohydrates or their hydrolyzed products, that the first matter of importance in studying these methods was a determination of the simplest means for estimating the quantity of copper precipitated.

For the determination of copper electrolytically, if many determinations are to be made at a time, the platinum apparatus becomes very expensive. If for this method, which when properly conducted gives excellent results, we can substitute a volumetric method giving equally good results, it would seem desirable to do so. A volumetric method for the estimation of the precipitated cuprous oxide is much to be preferred to any gravimetric method, provided that it gives results of the same degree of accuracy. We offer the following method which in our hands has given excellent results:

100 cc. of Fehling's solution are diluted with 100 cc. of water and heated in a boiling water-bath. A known amount of sucrose or starch contained in carefully analyzed samples which are as nearly as possible like the substance under analysis, is inverted.

These solutions are used with similar solutions containing approximately known amounts of sucrose or starch. The amounts taken in each case are such that the precipitated cuprous oxide is nearly identical in weight. The precipitated cuprous oxide is collected on a Hirsch funnel covered with asbestos felt. After washing thoroughly with water the top layer of the asbestos carrying most of the cuprous oxide is transferred with a platinum spatula to the beaker in which the precipitation was made. The remaining asbestos is moistened and the cuprous oxide adhering to the side of the funnel is easily rubbed off. Water is added and the mass thoroughly stirred. Fifty cc. of a saturated solution of ferric sulphate in twenty per cent. sulphuric acid is added. After the cuprous oxide is dissolved, filter on the same funnel, thus leaving it ready for another filtration. The solution is then ready for titration with potassium permanganate. The end-reaction is clear and definite.

The possible objections to be urged against the use of a volumetric method are: First, the possibility of oxidation of the cuprous oxide; second, the possible re-solution of the oxide. This is equally an objection to any gravimetric method, should it occur, but our investigations proved that no such re-solution occurs. A third objection may be made that the results are not strictly comparative. The experiments made bear directly upon these points.

As to the oxidation of cuprous oxide, six lots containing equal quantities of invert sugar were treated as usual. Three of these lots were filtered, washed, dissolved, and titrated at once with permanganate. 47.00, 47.10, and 47.15 cc. were required, an average of 47.10 cc. The remaining three lots were treated as above, except that instead of being dissolved at once they were allowed to remain for three hours on the filter, then removed and kept under water over night. The next day they were dissolved and titrated, requiring 47.15, 47.10, and 47.00 cc. respectively, an average identical with the results obtained where every possible precaution was taken against oxidation.

When the precipitated cuprous oxide was allowed to stand in the alkaline solution from which it was precipitated, instead of filtering immediately, the following results were obtained:

In the case of immediate filtration and titration, 41.4, 41.4, and 41.5 cc., being an average of 41.43 cc. of permanganate solution, were required, while for the oxide which stood twenty-four hours in the alkaline solution from which it was precipitated before it was filtered, there was required 41.5, 41.7, and 41.3 cc. permanganate, the average of which, 41.5 cc., is almost identical with the preceding value. This indicates clearly that no re-solution takes place. While in ordinary work it is not necessary to allow these precipitates to stand more than twenty-four hours before treatment, it might occasionally be necessary, however, to allow them to stand over night; this could be done with safety.

The following results will show that under proper manipulation, it is possible to get figures which are perfectly harmonious among themselves. Sugar solutions were made which would contain, on inversion, the starch or invert sugar equivalent of 0.38 gram of sucrose. This solution required, when the cuprous oxide was precipitated by Allihn's method, an average of 41.3 cc. of potassium permanganate solution, while the average obtained by precipitating the oxide in a boiling water-bath for one-half hour was 41.47 cc. Three different solutions, inverted independently, were used. These required for the first method 41.1 cc.; 41.3, 41.2 cc.; and 41.4, 41.5 cc., respectively, while for the water-bath precipitation 41.4, 41.5 cc.; 41.4, 41.7 cc.; and 41.5, 41.3 cc. were required. With a commercial starch the results were, by Allihn's method of precipitation, 34.5, 34.7, and 34.6 cc.; and by the water-bath 34.8 and 35 cc.

It will be noticed that these results are remarkably close together, that while the water-bath precipitation gives somewhat higher results, that as a whole these figures are as consistent and harmonious as analytical results generally are, and that the extreme error is very slight.

The constant checking of results in compounds of unknown carbohydrate content against those obtained from substances of known composition, places each chemist, after he has become familiar with the manipulation, where he is entirely independent of the possible influences of local climatic conditions. Our own work shows that one can constantly obtain the same percentages with the same reducing solutions. Of course we appreciate the fact that it is difficult to constantly obtain, from complex carbohydrates, solutions having constant reducing power, and on this account we have taken substances which were easily hydrolyzed to a constant reducing power.

Our purpose has been to deal in this paper only with the determination of the reduced copper. The amount of dextrose calculated to copper according to the ratio $5Cu_2O : 2C_6H_{12}O_6$ is 1 mg. Cu = 0.5678.

An inspection of Allihn's tables will show that, while the values given at the beginning of the table for weights not far from ten milligrams of copper is higher than that calculated from the reaction, that it soon begins to drop and for 100 milligrams it reaches its lowest point, namely, 0.509 milligram of dextrose for one of copper, which is much lower than the calculated weight; from this point the ratio steadily rises until at the highest point in copper weight the table reaches, 463, the dextrose equivalent 249.9 gives a ratio of 1 : 0.539.

A calculation of the amount of dextrose or its equivalent in unknown mixtures corresponding to potassium permanganate as given by the ratios $2C_6H_{12}O_6 : 5Cu_2O$; $10Fe : K_2Mn_2O_8$ gives, as would be expected, results entirely too high.

Our method for overcoming this difficulty is to take a known amount of pure cane-sugar as a standard for sucrose and for starch a commercial starch which has been very carefully analyzed, and treat this under exactly similar conditions with the substances containing approximately known amounts of sugar or starch. Thus we always get nearly the same weights of suboxid in all cases, and inasmuch as we determine each time our sucrose or dextrose ratio, any variation of climatic condition can hardly affect results. In this connection it has seemed to us that the variation in boiling-point due to the locations of laboratories at different altitudes might seriously affect the direct use of Allihn's tables. Unfortunately our weights of cuprous oxide were so high (they were made so intentionally to avoid multiplying errors), that we could not make this comparison by use of results now in our possession, but we shall make it a point as early in the future as possible, to investigate this matter. Our laboratory is over 4800 feet above sea-level, the average barometric pressure 637 millimeters, and the boiling-point close to 95°. This difference of 5° in the boiling-point may be well supposed to have its effect.

Another point has occurred to us: our results by permanganate have led us to suspect that all the copper may not be present in the precipitate as cuprous oxide. We are satisfied that after precipitation, and until acted upon by the ferric sulphate solution, no oxidation of the precipitate takes place, yet we find more copper by the electrolytic method than by the permanganate. The ratio is 1 : 0.9905. It may be urged that this represents the error due to the determination of the cuprous oxide by the permanganate method, but we are unwilling to concede this. However, even were this granted, the admission would not affect the accuracy of the method we offer, for correct results depend only upon the permanganate factor, and not upon the absolute amount of copper.

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[CONTRIBUTIONS FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, No. 36.]

THE ATOMIC MASS OF TUNGSTEN AND THE PREPARATION OF SODIUM PERTUNGSTATE BY MEANS OF THE ELECTRIC CURRENT.[1]

BY GEORGE EDWARD THOMAS.

Received January 5, 1899.

I. THE ATOMIC MASS OF TUNGSTEN.

THERE have been numerous determinations of the atomic mass of tungsten made in this laboratory; but as there were noted discrepancies in the results obtained, it was deemed advisable to pursue further investigation, as there appeared to be a probability that an examination of the trioxide of tungsten from different sources might reveal the cause of the disagreement mentioned.

Scheelite from Schlackenwald, Bohemia, and wolframite from Monroe county, Connecticut, were treated independently as follows: The finely divided minerals were digested for several days with *aqua regia*, and the insoluble residue washed repeatedly with water, and subsequently treated with ammonium hydroxide. These solutions were then evaporated and the crystals obtained were ignited, and to remove any molybdenum which might be

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[1] From the author's thesis for the degree of Doctor of Philosophy.

present, the trioxides were exposed in a porcelain boat to the action of hydrochloric acid gas at a gentle heat in a tube of hard glass.

After the reignition of the oxides, they were placed in a porcelain dish, covered with distilled water, and ammonia gas introduced until complete saturation was attained. These salts were repeatedly crystallized until perfectly white.

It appeared desirable, before further work was undertaken, to submit portions of the two oxides to Dr. W. L. Hardin, for examination, as he was, at the time of this research, determining by means of elaborate apparatus the atomic mass of tungsten by reduction of the trioxide in hydrogen gas and subsequent reoxidation of the metal.[1]

Reduction of tungsten trioxide obtained from wolframite from Connecticut:

	Weight of WO$_3$. Grams.	Weight of W. Grams.	Atomic mass of tungsten.
1	3.14520	2.49330	183.58
2	3.10516	2.46141	183.51
3	4.17792	3.31244	183.83
		Mean,	183.64
		Maximum difference,	0.32

Oxidation series:

	Weight of W. Grams.	Weight of WO$_3$. Grams.	Atomic mass of tungsten.
1	2.48088	3.12790	184.05
2	2.44588	3.08318	184.22
3	3.29370	4.15260	184.06

Experiments on material from scheelite from Bohemia. Two reductions were as follows:

	Weight of WO$_3$. Grams.	Weight of W. Grams.	Atomic mass of tungsten.
1	2.77363	2.19950	183.89
2	2.13327	1.69120	183.63

The oxidation gave:

	Weight of W. Grams.	Weight of WO$_3$. Grams.	Atomic mass of tungsten.
1	2.18985	2.76060	184.17
2	1.68208	2.12070	184.08

These investigations prove conclusively that the trioxides from both minerals were identical, and that the errors alluded to were not to be attributed to the difference in the sources of the minerals examined, and as it was evidently unnecessary to

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[1] This Journal, 19, 657 (*1897*).

confirm his observations, further study in this particular direction was discontinued.

In the belief that there was something present in the mineral, or in the method for obtaining the material for analysis, which caused the lack of concordance in the results, another line of procedure was adopted.

.1648 grams of finely pulverized wolframite, from Zinnwald, Bohemia, were fused with four times their weight of sodium carbonate in a wind furnace. Iron crucibles were employed, but the intense heat melted the crucibles, with an incidental loss of material, requiring the use of fire-clay vessels.

The fusion of unattacked oxides, sodium tungstate, and sodium carbonate, was lixiviated with water, and the solution of the sodium salts siphoned off. A purification by means of fractional crystallization was attempted; at least sixty crystallizations were made covering a period of about two months. Large quantities of silica were separated, which was introduced partly by the use of fire-clay crucibles. After this prolonged treatment the sodium tungstate, although perfectly white and apparently pure, contained a trace of sodium carbonate and silica.

However, the results from the water of crystallization, by heating the salt in an air-bath at temperatures varying between 180° and 200° C., were so concordant that it appeared probable that this might prove to be a reliable method for ascertaining the atomic mass of tungsten.

Preliminary investigation:

$$H = 1.008 \qquad O = 16 \qquad Na = 23.05$$

In this series of experiments calibrated weights were not employed and a Troemner balance was used, suited for ordinary analytical work.

	Weight of salt. Grams.	Weight of water. Grams.	Per cent. water.	Atomic mass.
1	1.4267	0.1558	10.92	183.82
2	2.1275	0.2323	10.91	183.86
3	2.3599	0.2582	10.94	183.19
4	6.8925	0.7534	10.93	183.50
5	3.2494	0.3554	10.94	183.30
6	4.4651	0.4880	10.93	183.55
7	7.1011	0.7759	10 93	183.63
8	11.0159	1.2057	10.94	183.07
9	9.3313	1.0194	10.92	183.69
10	8.1501	0.8912	10.93	183.38

The difficulty encountered in the separation of sodium tungstate from sodium silicate indicated the necessity of abandoning this material for further use for atomic mass determinations.

Therefore, to test the accuracy of this method, ammonium tungstate from scheelite, from Bohemia, and wolframite, from Connecticut, purified as already described, were ignited, and the trioxide obtained was dissolved in sodium hydroxide prepared by dissolving metallic sodium in distilled water in a platinum dish. This solution was evaporated to crystallization; after repeating this operation three times the salt was found to contain sodium carbonate, due to absorption of carbon dioxide from the air, caused by the excess of sodium hydroxide. It was dissolved in distilled water and decomposed by electrolysis in an apparatus described on page 378. The greater portion of the sodium hydroxide in the outer compartment was added to the contents of the bulb; the remainder was rejected in order that there might be no excess of sodium hydroxide present. This solution was evaporated to crystallization, the salt dissolved, filtered and recrystallized. The product was examined for silica, carbon dioxide, and ozone, with negative results.

These crystals of sodium tungstate were white, and upon analysis yielded 70.274 per cent. of tungsten trioxide, the theoretical value, on a basis of 184 as the atomic mass of tungsten, being 70.303 per cent. Varying the conditions of temperature produced different results, indicating that all of the water was not eliminated at 200° C., and at much higher temperatures volatilization ensues. Therefore 0.7903 gram of the salt was heated for one-half hour at 220°, allowed to cool, and weighed, the loss indicating 10.85 per cent. water. Repeated experiments were made with a corresponding increase in temperature and loss, until between 264°–294° C., when no loss in weight was observed, and the percentage of water found equaled 10.907, the theoretical on a basis of 184 for the atomic mass of tungsten being 10.909. Upon sintering the salt in a platinum crucible there was a loss of 11.03 per cent. in weight, and when the covered crucible is kept at a red heat for some time, a white substance is noticed on the lid. There were also four determinations made by heating the salt in a tube of glass, and collecting the water in a U-tube containing sulphuric acid and pumice stone, the results confirming the belief that volatilization accompanied an increase of temperature. The following atomic mass determinations were made by heating the normal salt between 268° and 295° C. A Troemner balance (sensitive to the fortieth of a milligram) and weights previously calibrated were employed.

FIRST SERIES.

	Weight of $Na_2WO_4.2H_2O$. Grams.	Weight of water. Gram.	Atomic mass.
1	1.36222	0.14842	184.507
2	1.06905	0.11638	184.852
3	1.40966	0.15366	184.421
4	2.34595	0.25556	184.628
5	1.00236	0.10913	184.822
6	1.12350	0.12236	184.710
7	1.19171	0.12963	185.116
		Mean,	184.722
		Maximum difference,	0.695

SECOND SERIES.

8	1.04092	0.11365	183.884
9	1.34561	0.14763	182.290
10	1.01077	0.10916	187.507
11	1.01065	0.11042	183.668
12	1.03371	0.11226	185.657

H = 1.008 O = 16 Na = 23.05

The results are not recorded in the order in which they were obtained. Those from one to seven inclusive are grouped together as indicating those which are most concordant, and consequently believed to most nearly approach the true atomic mass.

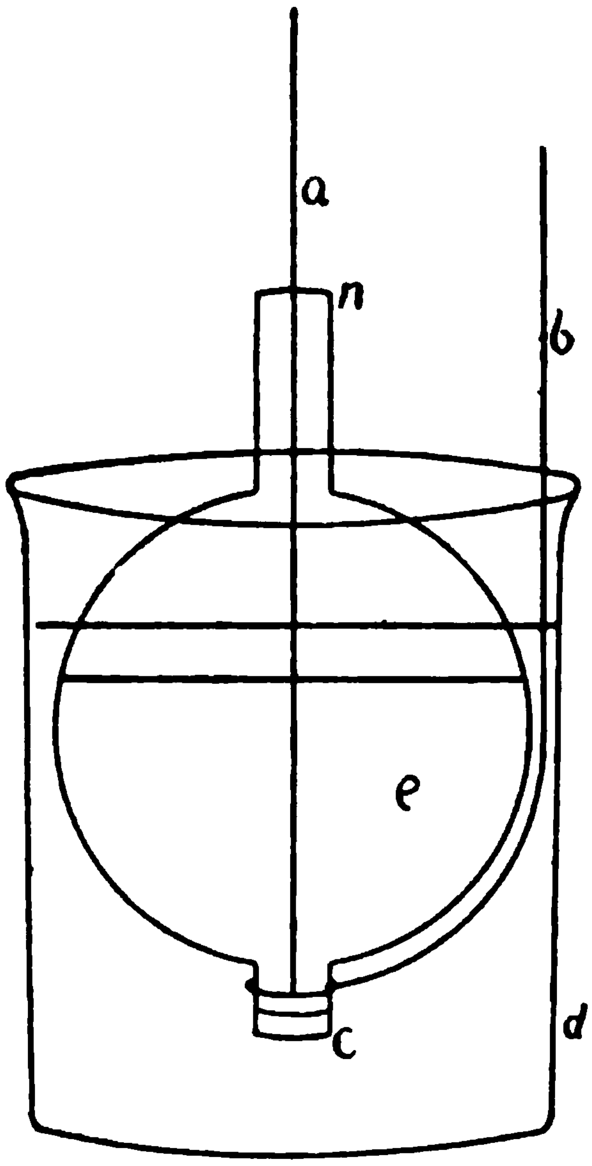
The marked discrepancies appear to have been incident to the difficulty of obtaining a uniform temperature in all parts of the air-bath. It was thought that a slight error might have been introduced by the presence of hygroscopic moisture in the air-dried salt. Upon allowing a portion to remain in a desiccator over calcium chloride for some hours, no appreciable loss in weight was observed.

The great difference between the molecular weight of water and the atomic mass of tungsten causes the slightest errors of analysis to seriously affect the results; which, in addition to the danger of volatilizing a portion of the material, appears to render the method unsuited for the determination of the atomic mass of tungsten.

II. SODIUM PERTUNGSTATE.

When sodium tungstate was electrolyzed in a platinum crucible, and the solution subsequently acidulated with hydrochloric acid, a gas was evolved which liberated iodine from a solution of potassium iodide. To further the investigation of this phenomenon, an apparatus was constructed to facilitate more complete oxidation, as this was believed to be the cause of the reaction observed upon the addition of the acid.

The figure represents the apparatus, one half actual size. The outer vessel, *d*, is a beaker glass; the inner compartment consists of a bulb with two openings, the lower aperture being covered with parchment, which is employed to prevent the solution of sodium tungstate from flowing into the beaker, *d*. By placing the finger over the opening, *n*, all of the solution subjected to the oxidizing action about the anode, *a*, may be separated without loss or contamination. The anode consists of platinum wire, while the cathode may be platinum, nickel, or iron, as it is not corroded.



E. Pechard[1] describes the preparation of a new oxygen compound of tungsten by the boiling of paratungstate of sodium with hydrogen peroxide, the solution acquiring, during the operation, a yellowish tint and yielding no precipitate upon the addition of nitric acid; the crystals obtained, to which he ascribed the formula $Na_2O.W_2O_7.2H_2O$, liberated chlorine from hydrochloric acid and iodine from potassium iodide. Experiments were first made with solutions containing an excess of alkali; but as acid solutions are more favorable to oxidation, varying quantities of acid were subsequently added to the solution of the sodium tungstate.

After numerous experiments extending over a long period, the best results were attained by employing a current which showed before the introduction of the electrolyte into the circuit, an amperage of one and four-tenths, and a voltage of 107. The electrolyte consisted of a solution of fifteen grams of sodium tungstate dissolved in fifty cc. water and one-half cc. acetic acid (twenty-five per cent.), a corresponding quantity of acid being added to the water in the beaker to facilitate the conduction, and a further addition of one-quarter cc. acetic acid, after four hours' contact, to the contents of the bulb.

During the operation much heat is generated, due to the resistance offered by the electrolyte; and the solution in the bulb as the salt approaches the para condition, caused by the alkali permeating the membrane and collecting about the cathode, acquires a yellow color. After six hours' treatment it will yield no precipitate upon the addition of nitric acid. The solution should then be removed from the bulb, as prolonged contact with the current will affect a complete decomposition with a subsequent separation of tungstic acid. The solution after this treatment is acid in reaction.

The yellow solution when evaporated on a water-bath below 100° C. becomes sirupy, retains its yellow color, possesses a very high specific gravity, and when allowed to crystallize, yields yellowish-white crystals. These were thought from their appearance and their reactions, namely, the liberation of chlorine from hydrochloric acid and ozone upon the addition of sulphuric and nitric acids, to be perfectly pure sodium pertungstate; but upon

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[1] *Compt. rend.*, 112, 1060–1062.

making determinations of oxygen in different samples, by the use of Bunsen's apparatus, collecting the chlorine liberated by boiling with hydrochloric acid, in a solution of potassium iodide, and titrating with a standardized solution of sodium hyposulphite, it was found that less than four-tenths of a per cent. of oxygen was present.

The work of Pechard indicated the presence of 2.82 per cent. to 2.93 per cent. of oxygen. These experiments gave positive proof that the oxidation in the diaphragm cell was not complete, due in all probability to the short interval that the current could act while the salt was in the para condition, as the composition of the contents of the inner bulb is constantly changing. Fractional crystallization was not applicable, owing to the readiness with which the oxygen compound and the other sodium tungstates dissolve in water. Attempts were made to affect its solution in various solvents: but chloroform, benzene, carbon disulphide, ether, and ethyl alcohol were without action. It was found that a ninety per cent. solution of methyl alcohol would dissolve the sodium pertungstate, but a portion of the contaminating salt was also soluble; however, this was largely eliminated.

Upon subsequent crystallization over calcium chloride, the yellow crystals liberated ozone while in the desiccator, indicating a partial decomposition; and upon experimenting, it was found that the method was inoperative as a means of separation. The possible oxidation of the alcohol would also render this treatment unsatisfactory. Before this knowledge was acquired attempts were made to prepare other pertungstates by double decomposition with salts of the metal; this, however, was abandoned after the impurities were discovered, and the efforts for their removal proved unsuccessful. After this work was completed an experiment was made using a more concentrated solution, and subjecting it to the action of a current of less intensity at a temperature below 20° C. Large quantities of ozone were evolved, and the solution, after subjecting it to the action of hydrochloric acid, only gave a faint test for chlorine, indicating that a higher temperature in this instance is more favorable to oxidation.

It may be noted that the oxygen in this compound is present as ozone, for upon ignition of the salt a gas was evolved which liberated iodine from potassium iodide. Hence, there is no doubt whatever that pertungstate of sodium was formed, and although the isolation of this substance was not accomplished, the preparation of the compound by this method is of great importance, as it shows an additional analogy to exist between tungsten and sulphur, the second member of this group.

While pursuing this work, a modification of this process suggested itself as an admirable means of preparing meta- or paratungstate of potassium or sodium. The only change necessary for the accomplishment of this result appears to be the elimination of the acid, and the use of a graduated beaker for the outer vessel. A definite quantity of the normal salt is introduced into the bulb. The diaphragm prevents the contamination of the outer liquid with sodium tungstate, as it was found that it did not permeate the membrane. Definite portions of the solution of the alkali may be removed from time to time, and titrated with normal acid until the requisite amount of alkali has been separated. The ozone present may be removed by heating from 200° to 400°. The crystals are dissolved and transformed into barium meta- or paratungstate by the addition of barium chloride.

The accuracy of this theory will be determined in the near future. From a theoretical standpoint, it appears to be better suited for the preparation of the salts mentioned than the methods now employed.

[CONTRIBUTIONS FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, No. 37.]

OBSERVATIONS ON DERIVATIVES OF ACONITIC ACID.

BY D. C. HANNA AND EDGAR F. SMITH.

Received January 5, 1899.

I. ACTION OF PHOSPHORUS TRISULPHIDE UPON ACONITIC ACID.

ACONITIC acid was prepared by the method of Hentschel.[1] One hundred and sixty-eight grams of it were then converted into the sodium salt, and portions of forty grams of this salt and eighty grams of phosphorus sulphide were intimately

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[1] *J. prakt. Chem.* [2], 35, 205.

mixed and heated in a distilling bulb. The vapors which were evolved, were conducted into water. This aqueous solution had an odor resembling that of naphthalene. Sodium hydroxide was mixed with it and steam was then conducted through the solution. Small quantities of a rather heavy oil passed over with the aqueous vapor. It was extracted from the water with ether. The ethereal solution was dehydrated with calcium chloride. The oil remaining after distilling off the ether weighed 0.2980 gram. Its alcoholic solution was mixed with an alcoholic solution of picric acid, when crystals separated which were identical with those of the picric acid derivative of thiophtene, obtained by V. Meyer.[1]

As the preceding method did not yield the thiophtene in very great abundance we mixed and distilled ninety grams of aconitic acid with 180 grams of phosphorus sulphide. The resulting vapors, as before, were conducted into water. A gentle heat was sufficient to start the reaction, which then proceeded with considerable violence. Much hydrogen sulphide was liberated. The distillate was again mixed with sodium hydroxide and steam was conducted through it. An oil passed over and was removed from the water with ether. It proved to be thiophtene and weighed 0.6975 gram. This is practically about the same yield of thiophtene as was obtained by V. Meyer on distilling citric acid with phosphorus sulphide. Our product boiled at 225°, while Meyer records the boiling-point of the purest thiophtene, made from citric acid at 224°–226°.

The second method seems on the whole preferable to the first method. Two grams of our thiophtene were dissolved in a little absolute alcohol, and to this solution were added two and five-tenths grams of picric acid in alcoholic solution. The characteristic yellow-colored picric acid derivative immediately crystallized out. The dried compound melted at 133°. It has the formula $C_6H_4S_2.C_6H_3O(NO_2)_3$. Portions of it were analyzed.

1. 0.2078 gram of the yellow crystals was oxidized with concentrated nitric acid. The sulphur, weighed as barium sulphate, equaled 0.0359 gram = 17.28 per cent. sulphur, instead of 17.34 per cent. sulphur.

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[1] Die Thiophen Gruppe, p. 250.

2. A nitrogen determination was made by the Kjeldahl method.

0.1972 gram substance gave 0.0221 gram of nitrogen = 11.20 per cent. nitrogen instead of 11.38 per cent. nitrogen required. The picric acid derivative gave a dark purple-red color with a warm solution of isatine.

II. ACTION OF PHOSPHORUS TRICHLORIDE UPON A CITRIC ACID ESTER.

Conen[1] allowed phosphorus trichloride to act upon triethyl citric ester and obtained, as he thought, triethyl aconitic ester. In the last edition of Beilstein's "Organic Chemistry", Vol. I, p. 817, in the description of triethyl citric ester the following statement occurs: "damit identisch (?) ist das Produkt aus Citronensäuretriaethyl Ester und PCl_3 bei 100°.

We prepared pure triethyl citric ester, boiling at 270° (295 mm.), and heated eleven grams of it in a sealed tube with four grams of phosphorus trichloride. The temperature of a water-bath was employed in heating the mixture. On opening the tube its contents were transferred to a distilling bulb and subjected to distillation under 295 mm. pressure. The fraction passing over at 252° was collected and redistilled. The boiling-point remained constant. The product was a heavy, colorless oil. It boiled at 274°–275° at the ordinary pressure, while triethyl citric ester under similar conditions boiled at 294°.

This oily liquid was taken up with water and boiled with barium hydrate. The excess of barium was removed with carbon dioxide and the filtrate concentrated. A hard glue-like mass, consisting of plates, separated. In every respect this salt was identical with barium aconitate. The acid liberated from it separated in forms like these of aconitic acid, and agreed with the latter in all of its physical properties. It dissolved very readily in anhydrous ether, thus proving that citric acid was absent as the latter is insoluble in this solvent. The evidence here presented supports the view that phosphorus trichloride converts triethyl citric ester at 100° into triethyl aconitic ester.

UNIVERSITY OF PENNSYLVANIA.

[1] *Ber. d. chem. Ges.*, 12, 1655.

[CONTRIBUTIONS FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, No. 38.]

ACTION OF HYPOPHOSPHOROUS ACID UPON MOLYBDIC ACID.

BY CLARENCE EBAUGH AND EDGAR F. SMITH.

Received January 5, 1899.

IT seemed to us a matter of some interest to learn to what degree molybdic acid could be reduced by hypophosphorous acid. With that end in view, 17.5 grams of very pure ammonium molybdate were dissolved in a liter of water, thus making an approximately tenth-normal solution of the trioxide. However, the real molybdenum content of this solution was ascertained by reducing a known volume of the liquid with zinc and sulphuric acid, and then reoxidizing with a standardized potassium permanganate solution. A one per cent. solution of hypophosphorous acid was employed to effect the reductions.

It was observed that when a concentrated solution of hypophosphorous acid acted upon a concentrated solution of molybdic acid, the liquid assumed at first a yellow and subsequently a brown color. If the solutions were, however, diluted no change in color was noticed in the cold, but upon the application of heat a deep blue color made its appearance. Upon adding a solution of potassium permanganate to this hot liquid the end-reaction was not well defined. If, however, the blue solution was cooled and then treated with permanganate, the end-reaction (complete decolorization) became sharp. The slightest excess of oxidant then occasioned the usual purple tinge. On standing, the liquid slowly regained a blue color, because, doubtless, of the reducing effect of traces of excessive hypophosphorous acid.

The titrations were conducted in solutions (*a*) made acid by a definite excess of hypophosphorous acid, (*b*) acidulated with sulphuric acid, and (*c*) neutralized with an excess of barium carbonate. Barium hypophosphite caused no reduction in the molybdate solution even when it was boiled. In one instance the cold, reduced solution was poured into a measured excess of potassium permanganate acidulated with sulphuric acid, and titrated back with a ferrous sulphate solution. The most satisfactory results were obtained in titrating the cold solutions, acidulated with sulphuric acid. They are recorded in the following table:

TABLE.

1.0 cc. solution = 0.01256 gram molybdenum trioxide.

I. MoO_3.	II. Weight MoO_3.	III. $KMnO_4$.	IV. 1 cc. $KMnO_4$ = 0.0006523 gram O. Wt. O represented by $KMnO_4$.	V. Weight Mo.	VI. Weight Mo_xO_y (subtract IV from II).	VII. H_3PO_2 (One per cent.)	VIII. Time boiled.	IX. Mo in VI.	X. O in VI.	XI. Ratio of Mo to O.
cc.	Gram.	cc.	Gram.	Gram.	Gram.	cc.	Minutes.	Per cent.	Per cent.	
25	0.31399	25.5	0.01663	0.20933	0.29736	5	15	70 39	29.61	
25	0.31399	20.5	0.01337	0.20933	0.30062	5	15	69.63	30.37	$Mo_2O_{5.2}$
25	0.31399	26.2	0.01709	0.20933	0.29690	5	30	70.50	29.50	
25	0.31399	29.1	0.01898	0.20933	0.29501	5	30	70.95	29.05	
25	0.31399	28.7	0.01872	0.20933	0.29527	5	60	70.89	29.11	
25	0.31399	28.5	0.01859	0.20933	0.29540	5	60	70.86	29.14	
20	0.25120	20.3	0.01324	0.16747	0.23796	4	60	70.37	29.63	
30	0.37680	31.0	0.02022	0.25120	0.35658	6	60	70.44	29.56	
							Mean	70.48	29.52	Mo_2O_5
								70.59	29.41	
								0.11	0.11	
1.0 cc. solution = 0.012836 gram molybdenum trioxide.										
20	0.25671	24.2	0.01579	0.17114	0.24092	4	—	71.07	28.93	
20	0.25671	24.2	0.01579	0.17114	0.24092	8	—	71.07	28.93	
30	0.38506	30.1	0.01963	0.25671	0.36543	6	—	70.25	29.25	
30	0.38506	35.1	0.02289	0.25671	0.36217	10	—	70.89	29.11	
25	0.32089	31.4	0.02048	0.21293	0.30041	6	35	70.87	29.13	
25	0.32089	35.6	0.02322	0.21293	0.29767	10	35	71.53	28.47	
35	0.44925	44.5	0.02903	0.29950	0.42022	8	37	71.27	28.73	
35	0.44925	50.3	0 03281	0.29950	0.41644	10	40	71.91	28.09	
20	0.25671	25.8	0.01683	0.17114	0.23988	4	45	71.34	28.66	
20	0.25671	26.5	0.01728	0.17114	0.23942	8	45	71.49	28.51	
20	0.25671	27.0	0.01761	0.17114	0.23900	8	45	71.58	28.42	
30	0.38506	43.0	0.02805	0.25671	0.35701	10	75	71.95	28.05	
30	0.38506	38.3	0.02498	0.25671	0.36008	10	60	71.29	28.71	
30	0.38506	40.1	0.02616	0.25671	0.35090	10	60	71.25	28.75	
20	0.25671	29.1	0.01898	0.17114	0.23773	10	60	71.94	28.06	
20	0.25671	32.3	0.02107	0.17114	0.23564	10	75	72.62	27.38	$Mo_2O_{4.52}$
							Mean	71.39	28.61	
								70.59	29.41	
								0.80	0.80	
25	0.32089	26.5	0.01729	0.21293	0.30360	10	60	70.35	29.65	
25	0.32089	33.8	0.02205	0.21293	0.29884	10	60	71.25	28.75	
25	0.32089	28.5	0.01859	0.21293	0.30230	6	60	70.43	29.57	
25	0.32089	27.2	0.01742	0.21293	0.30315	6	60	70.23	29.77	
							Mean	70.56	29.44	Mo_2O_5
								70.59	29.41	
								0.03	0.03	
							Mo_2O_5 requires theoretically	70.59	29.41	

In carrying out the determinations a measured quantity of the molybdic acid solution was introduced into an Erlenmeyer flask. This was followed with a definite volume of hypophosphorous acid of known strength. The mixture was then diluted to 150 cc. with water, and boiled on a stove plate for a definite period. After this the solution was chilled and immediately titrated with the permanganate solution.

An examination of the results warrants the conclusion that hypophosphorous acid reduces molybdic acid to the pentoxide (Mo_2O_5), and further that the method can not be regarded as applicable for trustworthy quantitative determinations of molybdenum.

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ON THE CONSTITUTION OF BARYTOCELESTITES.[1]

BY C. W. VOLNEY.

Received January 5, 1899.

ON a former occasion[2] I presented the result of analytical work and investigations on barium and strontium minerals occurring in the crystalline limestone of Eastern Ontario. I now have the honor to report on the analysis of a fourth species of these minerals from the same locality.

In the previous report, I have described the analytical methods. The principal interest may be found in the deductions and conclusions which follow the chemical work.

To judge from current literature, opinions seem to be uncertain as to the composition or existence of barytocelestites. Rammelsberg[3] states that Thomson's barytocelestites from the Lake Huron district was found by Professor Hunt to be free from barium. Dana, in his system,[4] is of the same opinion, and in the sixth edition[5] mentions merely the analyses, showing celestites with varying amounts of barium sulphate.

The celestite from Lansdowne, Eastern Ontario, reported from my analysis in 1891 as containing over three per cent. of barium sulphate, was likewise found by the analyst of the Canadian Geological Survey to be pure strontium sulphate, with only

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[1] Read at the New York meeting of the American Chemical Society, December 28, 1898.

[2] This Journal, 13, 290 (*1891*).

[3] Rammelsberg, Mineralchemie, 2d edition, p. 255.

[4] Dana's System, V, p. 620.

[5] Dana's System, VI, p. 906.

a trace of barium sulphate.[1] This is the same mineral which had been formerly[2] noted by Professor Hunt as barite.

So far, then, although various mixtures of barium sulphate and strontium sulphate have been mentioned as existing in minerals, we know of no definite occurrence of minerals constituted of these two sulphates.

The mineral, which I now place before you, gave on analysis the following results:

	Per cent.
$BaSO_4$	30.850
$SrSO_4$	70.010
Al_2O_3 Fe_2O_3	0.005
CaO	....
MgO	....
H_2O	....
	100.865

It occurs also in the Silurian crystallized limestones of Eastern Ontario, and is usually mentioned as fibrous, radiated celestite.

The mineral, reported upon previously, consisted practically of

$BaSO_4$	39.850
$SrSO_4$	58.200
	98.050

Their constitution may be thus represented:

	Calculated.	Found.
$BaSO_4$	39.026	39.850
$(SrSO_4)_2$	60.974	58.200
	100.00	98.050

	Calculated.	Found.
$BaSO_4$	29.67	30.850
$(SrSO_4)_3$	70.24	70.010
	100.00	100.860

The sulphuric acid of these minerals determined from the alkaline sulphates gave the following results:

Barium sulphate. I.	Barium sulphate. II.
1.179	1.203
1.186	1.198
0.163	1.201

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[1] Report of the Geological Survey of Canada (*1894*.)

[2] Report of the Geological Survey of Canada (*1863–1867*.)

or an average of 1.176 and 1.201, which makes the percentage of sulphur trioxide in either as follows:

I	40.03	40.377
II	40.89	41.23

From these data, the constitution of these two minerals may be expressed as

$$\text{I. } (BaSr_2)(SO_4)_3. \quad \text{II. } (BaSr_3)(SO_4)_4.$$

The four minerals collected from the above-named districts, have the following specific gravities:

	Sp. gr.
Barite	4.3989
Celestite	4.410
Barytocelestite, I	4.188
" II	4.123

The celestite and the two barytocelestites afford well-defined and distinct crystals. As they differ more or less from each other, although both of orthorhombic crystallization, the differences in crystallization may lead to some conclusion as to the influences, which different equivalent proportions of the strontium sulphate may have upon their isomorphous relation to each other. I hope to be enabled to lay these crystallographic relations before you at an early date, and thus conclude this investigation.

NEW YORK, December 17, 1898.

NOTES.

The Determination of Arsenic in Glycerine.—Mr. G. E. Barton has called my attention to the fact that in my outline of his paper on this subject, I quoted only one of the methods used by him, and neglected "to state that a direct addition of the glycerine (without charring) to the reduction flask was finally used as more accurate." Mr. Barton considers that this should be accepted as his method. A. C. LANGMUIR.

Corrections in Baumé's Hydrometer Tables.—I am advised by Mr. G. E. Barton of three errors in the hydrometer tables printed in the March number. On page 127 at 28.6° read '0.8827' instead of '0.8821', and at 36.3° read '0.8419' instead of '0.8418'; on page 132 at 75.0° read '0.6829' instead of '0.6830'. Mr. Barton also states that he has checked all the figures except those for the eighths of degrees; this fact will doubtless add to the confidence in the accuracy of the tables. SIDNEY S. EMERY.

VOL. XXI. [MAY, 1899.] NO. 5.

THE JOURNAL

OF THE

AMERICAN CHEMICAL SOCIETY.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WESLEYAN UNIVERSITY.]

THE USE OF COMPRESSED OXYGEN IN ELEMENTARY ORGANIC ANALYSIS AND OF SODA-LIME IN THE QUANTITATIVE DETERMINATION OF CARBON DIOXIDE.

BY FRANCIS G. BENEDICT AND OLIN F. TOWER.

Received October 22, 1898.

THE ordinary method of elementary organic analysis in which use is made of air and oxygen contained in a gasometer, suffices where but few determinations are to be made. The manipulation is, however, too lengthy to permit of rapid work, and having occasion to make carbon and hydrogen determinations in a large number of foods used in connection with experiments with a respiration calorimeter in this laboratory, it was necessary to modify materially the method so as to increase its rapidity. The method formerly employed is essentially the same as that described in most text-books on organic analysis, and may be briefly outlined as follows:

Oxygen obtained by heating a mixture of potassium chlorate and manganese dioxide was collected over water in a Mitscherlich gasometer. It was then freed from carbon dioxide, and dried as it entered the combustion tube. The substance was burned in the usual manner in a tube filled with granular copper oxide. The resulting water was collected in a tube containing glass wool drenched with sulphuric acid, and the carbon dioxide was absorbed in a potash bulb, which was followed by a small sulphuric-acid tube to collect the water coming over from the potash solution. On the end of a series of absorption tubes, a small U-tube was placed containing fused calcium chloride to absorb the moisture of the air in case of back suction. After the substance was completely burned and oxygen had been passed through, the tube was swept out with a current of air to remove all oxygen from the system.

There are several disadvantages in obtaining oxygen by the above method. The time consumed in generating and collecting the gas is considerable. Impurities present in manganese dioxide cause the formation of some carbon dioxide, which mixes with the oxygen and necessitates special care in purifying the gas before use. The oxygen standing in the gasometer over water becomes saturated with aqueous vapor. In order to remove all traces of carbon dioxide and water vapor it is necessary to pass the oxygen through the purifying apparatus very slowly. Furthermore, owing to the large quantities of these impurities present, the materials used in purification, *i. e.*, potassium hydroxide and sulphuric acid respectively, require frequent replenishing.

The use of Pepys or Mitscherlich gasometers for holding oxygen is an almost universal practice. These gasometers, if constructed of metal, soon leak owing to the attacks of acid fumes and vapors always present in a laboratory, and are constantly needing repairs. Glass gasometers do away with the large mass of metal, but rely on metallic pipes, cocks and connections to receive and deliver the gas. These connections are equally liable to the attack of acid, resulting in leakage and consequent loss of gas. The fragile nature of such gasometers and the necessity for transportation to the sink when being filled, make their handling difficult. Finally, the original cost of such an apparatus is not inconsiderable.

To overcome these disadvantages use is made of compressed oxygen in steel cylinders. Progress in the compressed air industry has reached such a point that it is comparatively easy to secure a strong, thoroughly well-tested cylinder of highly compressed oxygen. These cylinders are made in all sizes, containing from a few gallons to 100 cubic feet of oxygen. For the laboratory, a cylinder containing ten cubic feet or seventy-five gallons is of convenient size. The oxygen thus compressed is of a high degree of purity. Formerly hydrocarbons were used to lubricate the machinery for compressing the gas, thereby causing contamination of the oxygen with volatile hydrocarbons, which introduced serious errors when the gas was used in elementary analysis. Manufacturers have, however, replaced the lubricating oils with graphite, thereby eliminating the undesirable impurities of gaseous hydrocarbons. In the several cylinders of oxygen tested in this laboratory, gaseous hydrocarbons, or at least any hydrocarbons, not completely absorbed by the sulphuric acid of the drying apparatus to be described beyond, were never detected.[1]

The oxygen in these steel cylinders is comparatively dry and free from carbon dioxide, so that its purification is easy to accomplish. The carbon dioxide is absorbed by soda-lime in a small U-tube.[2] Owing to the small quantity of carbon dioxide present, one tube of this sort will remove this impurity completely for over twenty-five combustions. The soda-lime tube is followed by the drying apparatus, consisting of a cylinder about twelve cm. high half filled with concentrated sulphuric acid, through which the oxygen bubbles, thereby indicating the rate of flow.

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[1] Oxygen compressed in this form was first used in this laboratory for making combustions with an Atwater-Blakeslee bomb-calorimeter. These bomb-calorimeters have been introduced into several laboratories, all of which, consequently, have a supply of compressed oxygen. For those laboratories not possessing a cylinder the following is appended: The price of a ten-foot cylinder is about ten dollars. The so-called "commercial" oxygen, which differs from the "medical" only in so far as it has been, perhaps, a little less thoroughly washed and purified, costs at the rate of ten cents per foot; *i. e.*, one dollar per ten cubic feet. This amount is not great compared with the cost of an ordinary Mitscherlich or Pepys gasometer. Inasmuch as the gasometers are used almost exclusively to hold oxygen, it will be seen that they are not indispensable to the ordinary laboratory supplied with a cylinder of oxygen. Ten cubic feet will last for a great many carbon and hydrogen combustions, while the advantage of using a cylinder of this gas in the lecture-room is obvious.

The writers would here express their obligations to Mr. A. K. Johnston of the S. S. White Dental Manufacturing Company, Princess Bay, N. Y., who has furnished much valuable information.

[2] This and all other U-tubes here mentioned were five inches long and five-eighths inch outside diameter, as this was found to be the most convenient size.

Following this is a small U-tube containing pumice stone drenched with sulphuric acid to retain any moisture, which may escape absorption. The cylinder usually absorbs all the moisture, so that no gain in weight of the U-tube is observed. When the oxygen is run at an abnormally rapid rate, the U-tube shows a slight gain, as was proved by an experiment in which the U-tube gained one and eight-tenths milligrams after the oxygen had been passing rapidly through the system for thirty minutes.

Inasmuch as the oxygen contained in the steel cylinders is under great pressure, some method of regulating the flow of gas, as it enters the combustion tube, must be devised. The expensive precision and reduction valves used ordinarily with these cylinders can be replaced by the following simple arrangement: A rubber tube leading from the cylinder connects with a T-tube, one end of which dips one inch under mercury in a small bottle fitted with a rubber stopper having two holes. The second hole is left open. A rubber tube connects the other end of the T-tube with the purifying apparatus, which is in turn connected by rubber tubing to the combustion tube. This last rubber tube is supplied with a pinch-cock. When the valve on the oxygen cylinder is opened slightly, the gas will flow out, and passing through the driers produce a bubbling in the sulphuric-acid cylinders. As yet no gas escapes through the mercury. If now, as is often the case, one wishes to regulate the flow of gas, the pinch-cock is closed until the desired rate of flow is secured. Any excess of gas now escapes through the mercury trap. It is always possible to adjust the valve on the oxygen cylinder finally, so as to prevent any appreciable loss of oxygen through the mercury.

The furnaces used are of the ordinary Bunsen pattern, and have twenty-six burners. A hard glass combustion tube was filled in the usual manner with granular copper oxide. The oxidized copper spirals used to fill the entrance end of the tube after introducing the substance to be burned, were made by winding moderately stout copper wire in layers around a glass rod until the desired size was obtained. Such spirals were found to be more durable than those made from copper gauze. Red antimony rubber stoppers were found to possess a marked superiority in withstanding heat over those of ordinary rubber, and they were, accordingly, used at each end of the combustion tube. All rubber connections were made with $\frac{5}{32}$-inch red antimony tubing.

The water formed during the process of combustion was absorbed as usual in a Volhard U-tube containing glass wool drenched with sulphuric acid. The absorption of the carbon dioxide was effected by passing the gas after leaving the sulphuric acid U-tube through a U-tube filled with specially prepared soda-lime, followed by a similar U-tube containing, in one limb, soda-lime, and in the other fused calcium chloride. This substitution of soda-lime for the usual absorbent of carbon dioxide, *i. e.*, potassium hydroxide, while by no means new,[1] has given such satisfactory results in our hands as to warrant publication.

Repeated tests of a most exacting nature have shown that soda-lime, prepared as described below, absorbs carbon dioxide more completely and rapidly than potassium hydroxide solution. Passing 150 liters of air containing three and five-tenths grams of carbon dioxide through a system of two soda-lime U-tubes and a final check U-tube containing glass beads drenched with barium hydroxide solution gave no turbidity in the last tube. The air was aspirated at the rate of 500 cc. per minute.[2] In another experiment[3] ordinary air from the room was drawn through one soda-lime U-tube, followed by a Drechsel gas-washing cylinder containing a strong barium hydroxide solution, at the rate of 2100 cc. per minute without noting any turbidity in the barium hydroxide solution. It is needless to add that these tests could in no way be duplicated, if potassium hydroxide solution were used. Obviously then, so far as the absorption of the carbon dioxide is concerned, there need be practically no limit to the rate at which the gas may be passed though the soda-lime tubes. As a matter of fact, in this method the rate of flow is regulated solely by the completeness of combustion. In case of back suction there was no liquid to look out for as when a potash solution was used. To prevent atmospheric moisture from being

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[1] See *Ann. Chem.* (Liebig), 285, 385.

[2] Preliminary Investigations on the Metabolism of Nitrogen and Carbon in the Human Organism, by W. O. Atwater, C. D. Woods, and F. G. Benedict. Bulletin 44, Office of Experiment Stations, U. S. Department of Agriculture, p. 28.

[3] This Journal, 20, 299.

absorbed when back suction occurred, a small sulphuric-acid tube completed the series of tubes.

As dry air passes through the carbon dioxide absorbent in any system of tubes, it carries with it varying quantities of moisture, which must be collected and weighed to secure the true weight of the absorbed carbon dioxide. Actual experiments show this amount of water lost from a soda-lime tube during a combustion to be on the average about one-fourth of that lost from an ordinary Geissler potash bulb. To collect this water from the soda-lime tube, one limb of a second U-tube is filled with calcium chloride, while the other is filled with soda-lime. The limb filled with soda-lime is connected with the first U-tube. Both tubes are weighed. In ordinary combustions the second tube rarely gains as much as two milligrams, while a sulphuric-acid tube following a potash bulb ordinarily gains from six to ten milligrams. To prove the complete retention of water by the calcium chloride, a sulphuric-acid U-tube was placed immediately following, and weighed before and after a combustion, and in no case was any gain in weight observed. An additional advantage of this second U-tube lay in the fact that the first tube could be completely used up without the fear that carbon dioxide might escape absorption. When the second tube gained much more than two milligrams, it was an indication that the first tube was exhausted, and it was accordingly replaced by a fresh tube. A fresh soda-lime tube can be used ordinarily for six combustions before becoming exhausted, while it is hardly safe to use a potash bulb more than twice.

The progress of the absorption of carbon dioxide by the soda-lime is also indicated by a marked change in color. The fresh soda-lime has a slightly yellowish tinge, while the portion converted to carbonate is pure white. With a potash solution no such indication is present, and one must rely solely on the increase in weight of the potash bulb. As the carbon dioxide is absorbed in one limb of the tube, a very marked line of advancement is noticed where the color change occurs. This line advances as the absorption proceeds, and the efficiency of any tube can be immediately ascertained by noting this change in color.

A not inconsiderable item in considering the relative merits of soda-lime and potassium hydroxide solution is the question of the expense of the potash bulbs. Compared with the U-tubes they are very expensive, and their fragile nature is a decided disadvantage. Where a large number of combustions are to be made, it has been found advantageous to have a number of these soda-lime U-tubes filled in advance, and fitted with one-holed rubber stoppers carrying small bent glass tubes plugged at the ends with short bits of rubber tubing and a piece of glass rod. These tubes can be weighed to the second decimal place and, when wanted, checked up accurately on the balance.

In order to still further shorten the time of making a combustion, sweeping out the oxygen with air after combustion was omitted. As the tubes were weighed originally filled with air, the oxygen filling them after combustion, should be replaced by air. This is accomplished after the tubes have been disconnected in the following manner : Air, purified by passing through a soda-lime U-tube and a sulphuric-acid U-tube, is drawn by gentle suction with the mouth through the tubes to be weighed. These air-purifying tubes are kept in readiness, so that very little time is consumed in the process. If the tubes were weighed filled with oxygen, the error would be almost inappreciable, since the empty space in the U-tubes is small, particularly as compared with the empty space in a potash bulb. Before each weighing, the tubes were wiped off lightly with a piece of cheese-cloth. Weighings were in each case made with a counterpoise. The ease with which a U-tube can be wiped, as compared with a potash bulb, is apparent.

It was found that time could be saved by using two furnaces. One person then gave all his time to watching the furnaces, while another person made the weighings and kept the tubes replenished. By thus utilizing about one-third of the time of a second man, an average of two combustions an hour could be made. The furnaces were both connected with the same oxygen cylinder by inserting a T-tube just beyond the mercury safety trap previously described. Each furnace was supplied with an independent set of drying and purifying tubes. This was necessary in order to observe the rate of flow of each current of gas. To test the efficiency of the apparatus and method, substances of known composition and purity, *i. e.*, cane-sugar and benzoic acid, were analyzed and the results are given in the following table:

Substance.	Amount used. Gram.	Carbon dioxide found. Gram.	Carbon		Water found. Gram.	Hydrogen	
			Found. Per cent.	Theor. Per cent.		Found. Per cent.	Theor. Per cent.
Cane-sugar..	0.2000	0.3075	41.94	42.10	0.1145	6.41	6.43
" " ..	0.2018	0.3111	42.05	....	0.1158	6.42	....
Benzoic acid	0.2058	0.5193	68.83	68.85	0.0911	4.95	4.92
" "	0.1738	0.4388	68.87	....	0.0780	5.02	....

The cane-sugar was obtained as rock-candy. This was dried, powdered, and dried again until there was no loss in weight. The benzoic acid was a chemically pure preparation of the market. It was melted and recrystallized twice before being used. No traces of moisture could then be found.

The above results, fair samples of many others, seemed to justify the use of this method for determining carbon and hydrogen in organic substances. As a direct application of this method, it will suffice to say that over eighty samples of foods have been burned, and the agreement of duplicates is, to say the least, remarkable. Agreement as close as 0.03 or 0.04 per cent. was often obtained. Obviously this agreement substantiates in no way the absolute determination of carbon and hydrogen, but it does imply that the method is easy and regular, presenting no great difficulties in manipulation.

One essential feature is the soda-lime. As ordinarily prepared and sold in the market, it is a mixture of sodium and calcium hydroxides fused and granulated. Its chief use has been as a drier for gases and for determining organic nitrogen. Such soda-lime has very little absorptive power for carbon dioxide. To absorb carbon dioxide readily the soda-lime must be moist. This moisture is best obtained by modifying the method of preparation. One kilogram of commercial caustic soda, "Greenbank Lye," is treated with 500–600 cc. water in an iron kettle forming a strong solution, or more properly a thin paste. While still hot, one kilogram of quicklime, coarsely powdered, is rapidly added, stirring constantly with an iron rod or piece of gas pipe. The lime is slaked by the water of the caustic soda solution, and soon the whole mass heats and steams up. While in this stage, it is advisable to keep the mass stirred and the lumps broken up. No outside heat is necessary, and as soon as cool the product may be placed in wide-mouthed bottles, and the corks sealed in with paraffin or wax. When cool, it should not be moist enough to show water as such, *i. e.*, no particle should glisten in strong light. If too dry, a small quantity of water can be readily added after the soda-lime is made, though the great danger lies in adding too much water, thereby making the lime too pasty for the most efficient absorption. We have made over fifty kilograms of such soda-lime in the past three years, and invariably secure a good product when using the above formula.

While moisture is essential in securing the complete absorption of carbon dioxide, the amount of moisture carried away from a soda-lime U-tube by an air current is, as has before been stated, much less than that brought away from a potash bulb. Assuming that the soda-lime here used is a mixture of the hydroxides of sodium and calcium, and that the normal carbonates are formed when carbon dioxide is absorbed, we could properly have two equations; *viz.*,

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O,$$
$$2NaOH + CO_2 = Na_2CO_3 + H_2O.$$

Thus one molecule of carbon dioxide absorbed liberates one molecule of water from the hydroxides. Accordingly, for every gram of carbon dioxide absorbed about four-tenths gram of water is liberated. In actual experimenting, however, but a very small portion of this water leaves the soda-lime U-tube. In one tube 2.7467 grams of carbon dioxide were absorbed and only 0.1378 gram of water left the soda-lime tube. The sodium carbonate formed appears to retain the major portion of the water hygroscopically. While the deca-hydrated sodium carbonate loses its water of crystallization readily, the anhydrous salt takes up water with great avidity, and it is to this that we must attribute the retention of so much water in the soda-lime tube. Were it possible to form the acid carbonates of sodium and calcium under these conditions, the water would be retained chemically, and in fact not liberated. To disprove this high improbability some of the white spent soda-lime was heated in a long tube to low redness with provision for absorbing any carbon dioxide given off, exactly similar to the absorbing apparatus used above in the case of combustions. The first soda-lime U-tube lost one and eight-tenths milligrams, while the second containing also calcium chloride gained one and six-tenths milligrams, which shows that no carbon dioxide was driven out of the spent soda-lime. A large amount of water was, however, given off, indicating that the white seemingly dry carbonate had really absorbed considerable water hygroscopically. The whitening in a tube is not, therefore, due to drying out. Experiment has also shown that moistening white, spent soda-lime does not increase its absorbent power for carbon dioxide.

Soda-lime prepared as outlined above is recommended as a general reagent for freeing gases from carbon dioxide, such as normal air in determining gas densities. As a reagent for the quantitative determination of carbon dioxide, both in elementary organic analysis and in air analyses, it has given excellent satisfaction. The air analyses were made in connection with the respiration calorimeter above referred to. It appears to be an excellent general substitute for potassium hydroxide solution in all cases where the solid form of reagent is not proscribed.

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THE DETERMINATION OF CARBON MONOXIDE, METHANE, AND HYDROGEN BY COMBUSTION.

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Received November 10, 1898.

IN the development of technical gas analysis the researches of Winkler, Hempel, Lunge, and others have given us many methods which are both rapid and exact and which yield results quite as satisfactory as those obtained by the classical methods of Bunsen. But for the determination of hydrogen and methane modern methods have been found to be far from satisfactory. The combustion of hydrogen and hydrocarbons by means of copper oxide is no longer used because of its inconvenience. The combustion of hydrogen by means of palladium asbestos is open to the error which may result from the partial burning of the methane present. The fractional combustion of hydrogen by palladium sponge and the absorption of hydrogen by palladium black are exact, but the palladium needs to be frequently removed from the tube and heated, to render it again active. The last three of these methods, moreover, leave the methane still to be determined, a detail which so prolongs the analysis as to exclude the methods from general adoption.

It was but natural that gas analysts should prefer to use some method by which both hydrogen and methane could be simultaneously determined, and the procedure which is now most frequently employed is the Hempel explosion method or some modification of it. In speed and convenience of manipulation this method leaves little to be desired. Unfortunately, however, the results are neither constant nor accurate, first because of the smallness of the gas volume which is exploded, any error being thus multiplied about eightfold, and second because of the danger of the formation of oxides of nitrogen. This last difficulty is largely avoided if the determination is carried out as Hempel directs, but in the employment of an explosion pipette in which the gases are confined between two glass stop-cocks, there is no way of judging of the violence of the explosion. This is a point of considerable importance, for if the explosion is too violent the formation of oxides of nitrogen is probable, while if too weak the combustion is liable to be incomplete. If the explosion is made with oxygen instead of air the danger of formation of oxides of nitrogen from the nitrogen originally present in the gas mixture is increased[1] and the violence of the explosion becomes so great that Gill, who recommends this procedure, divides the explosion into two parts, using half of the required oxygen in each.

It seemed necessary, therefore, in seeking to improve the procedure for the determination of hydrogen and methane, to devise some method which would permit of the use of large volumes of gas and would so diminish the violence of the union of oxygen and the combustible gases as to reduce to a minimum the possibility of injury to the operator, and the probability of the formation of oxides of nitrogen. It was apparent that to attain these ends it would be necessary to abandon the method of explosion and to replace it by some form of slow combustion. The gris-

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[1] See the researches of Bunsen and Hempel upon this point.

oumeter devised by Winkler seemed to be an apparatus which might be adapted to this purpose provided that it were found possible to attain complete combustion without mixing the combustible gases and the oxygen *before*[1] their introduction into the grisoumeter. This proved to be feasible.

The determination of carbon monoxide by absorption with cuprous chloride offers many difficulties. The absorbent is somewhat difficult to prepare and keep, and the absorption can be completed in a reasonable time only by using two solutions of cuprous chloride and bringing the gas and the reagent into intimate contact by vigorous shaking.[2] Vignon[3] and later Noyes and Shepard[4] have avoided this absorption of carbon monoxide by exploding the gas simultaneously with the hydrogen and methane and then determining the contraction, the volume of carbon dioxide formed, and the oxygen consumed in the explosion. As will be seen below this procedure can also be carried out with satisfactory results by means of the combustion method which is here described.

The apparatus used for the combustion of the various gases is quite similar to the "grisoumeter" described by Winkler[5] and was made from a Hempel simple gas pipette for solid and liquid reagents[6] by cutting off the upper bulb and attaching in its place, by means of a rubber tube, a level bulb like that used by Hempel in his explosion pipette.[7] Through the opening of the single-hole rubber stopper *a* there passes a glass tube *b* which is open at both ends and contains an iron wire *c* three mm. in diameter. Another iron wire *m* of about one and five-tenths mm. diameter is pushed through the stopper and is then wound several times around the glass tube and cut off at the same height as the larger wire. This arrangement of the conducting wires is preferable to that suggested by Winkler, since the relative positions of the wires remain unchanged when the stopper

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[1] Mixing the oxygen and combustible gases before passing them into the grisoumeter was not attempted, for the combustion has been known to pass back through the capillary and explode the main mixture with most deplorable results.

[2] See Dennis and Edgar: This Journal, 19, 859.

[3] *Bull. Soc. Chim.*, *1897*, p. 832.

[4] This JOURNAL, 20, 343.

[5] *Ztschr. anal. Chem.*, 28, 288; Hempel: Methods of Gas Analysis, p. 236.

[6] Hempel: Methods of Gas Analysis, p. 35, Fig. 21, *b*.

[7] *Ibid.*, p. 103, Fig. 44.

is pushed into place and, as will be seen later, the use of a cement of any sort is avoided. The upper ends of the iron wires are connected by a platinum spiral *d*, contact between the platinum and iron being effected by simply wrapping the platinum wire several times around the iron wires. The platinum wire is one-fourth mm. in diameter and the coil into which it is bent is about two mm. in diameter and contains from twenty to thirty turns. After the spiral has been attached to the iron wires it is bent into the form of a horizontal S. Below the rubber stopper the smaller iron wire is fastened directly to the double binding-post P. The opening between the large iron wire and the tube through which it passes is closed air-tight by means of a piece of small rubber tubing carefully wired in place. The lower end of the iron wire is connected, by means of a binding-screw *e* and a piece of suitable wire, to the second binding-post P_2. Both binding-posts P_1 and P_2 should be insulated from the iron stand.

Fig. 1.

After the rubber stopper carrying the spiral has been inserted in place and the iron wires have been connected with the binding-posts, the pipette and capillary are filled with mercury by raising the level-bulb, the pinch-cock *g* on the rubber tube on the capillary is closed, and suction is applied to the tube *t* of the level-bulb by means of a water suction-pump. The air contained in the glass tube *b* is thus removed and the tube remains completely filled with mercury.

The gas volumes were measured in a simple Hempel burette[1] provided with a water-jacket (see Fig. 2). Mercury was used as the confining liquid and a drop of water was introduced into the burette to insure the complete saturation of the gases with moisture.

Fig. 2.

The method of procedure which was finally adopted for the combustion of the gases is as follows:

The combustion pipette is first completely filled with mercury by raising the level-bulb, and a measured quantity of the gas to be burned is then introduced. A quantity of oxygen more than sufficient to completely burn the gas is drawn into the gas burette and its volume noted. The burette is then connected with the pipette by the usual bent capillary tube (see Fig. 2) and the level-bulb of the pipette and the level-tube of the burette are placed at such heights that the gases in both pipette and burette are approximately under atmospheric pressure. A screw pinchcock *k* which has previously been placed upon the rubber tube joining the burette with its level-tube is now tightly screwed down so as to prevent, for the present, any movement of the mer-

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[1] Hempel. Methods of Gas Analysis, p 22, Fig. 17.

cury in the burette. The level-tube is now placed at such a height that when the screw pinch-cock *k* is opened the mercury will rise to the top of the burette but will not pass over into the pipette. The pinch-cocks *o,o* on the connections between the burette and pipette are now opened and the electric current, which should be just strong enough to maintain the spiral at a red heat, is turned on. Any electrical apparatus furnishing a current of sufficient strength to heat the platinum spiral to redness may, of course, be employed. If the current from a dynamo or storage battery is at the operator's disposal, the arrangement shown in Fig. 2. can be recommended as being both simple and convenient. The current is passed through the resistance frame F. (We have used a small frame carrying German silver wire about one and five-tenths mm. in diameter.) The terminals on the combustion pipette are connected with the frame by means of the flexible wires *V* and *W*, the ends of these wires being simply hooked into the coiled wire of the frame. The current passing through the platinum spiral can then be varied at will by simply hooking the end of *W* into the resistance coil at a greater or less distance from *V*.

When the spiral has been brought to the proper temperature the screw pinch-cock *k* is carefully opened and a slow and steady current of oxygen is passed over into the pipette. From ten to twenty cc. of oxygen per minute may be introduced, but the amount is, of course, somewhat dependent upon the length and temperature of the spiral. The combustion takes place quietly without the appearance of a flame and if the operation is properly conducted there is no possibility of an explosion since the combustible gas and the oxygen are in separate vessels and are made to combine as fast as they mix. Nevertheless a screen of heavy glass is always placed between the pipette and the operator to insure protection for the face in case of possible accident.[1] After the oxygen has been passed into the pipette, the spiral is kept at a red heat for about one minute to insure complete combustion of the gas. When, however, hydrogen alone is being burned, the combustion is complete almost as soon as sufficient oxygen has been introduced. When the combustion is finished

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[1] This precaution is invariably taken in this laboratory in all combustion or explosion analyses of gas mixtures.

the residual gas is passed back into the burette and measured.

The volume of gas which may be taken for the combustion is limited only by the capacity of the measuring burette, but for convenience in handling neither the combustible gas, the oxygen required, nor the residue after combustion is allowed to exceed 100 cc. The volume of gas in the pipette at any time during the combustion should be sufficient to prevent the mercury from rising and covering the spiral, or short-circuiting the current. This would take place if pure hydrogen were burned by adding pure oxygen, but the difficulty in this case is avoided by introducing into the 100 cc. of hydrogen about 95 cc. of a mixture of equal parts of oxygen and air.

In the following tables are given the results obtained with this apparatus in the determination of hydrogen and carbon monoxide and in the analysis of the residue of illuminating gas both before and after the removal by absorption of carbon monoxide. No corrections were made for the slight changes in temperature and barometric pressure which may have taken place during the progress of any one determination.

HYDROGEN.

The hydrogen was made by allowing hydrochloric acid to act upon zinc[1], the vapors of the acid being removed by shaking the gas with a strong solution of potassium hydroxide.

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.[2]
	cc.	cc.	cc.	cc.	cc.	cc.	cc.	cc.	cc.
Hydrogen taken	99.6	100.0	98.6	99.8	99.4	95.35	97.5	51.15	35.0
Oxygen and air added	99.6	99.95	99.9	100.0	99.1	96.6	99.75	48.95	100.0
Total	199.2	199.95	198.5	199.8	198.5	191.95	197.25	100.10	135.0
Residue after combustion	50.0	50.1	50.8	50.55	49.7	49.1	51.2	23.4	82.65
Contraction	149.2	149.85	147.7	149.25	148.8	142.85	146.05	76.7	52.35
Equivalent to hydrogen	99.47	99.9	98.47	99.5	99.3	95.23	97.37	51.13	34.9
	Per ct.	Per ct.	Per ct.	Per ct.	Per ct.	Per ct.	Per ct.	Per ct.	Per ct.
Hydrogen found	**99.9**	**99.9**	**99.9**	**99.7**	**99.9**	**99.9**	**99.9**	**100.0**	**99.7**

CARBON MONOXIDE.

This was prepared by heating together oxalic and sulphuric

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[1] Cf. Cooke and Richards : *Am. Chem. J.*, (*1888*), 10, 100.

[2] In IX and X air alone was added, and smaller amounts of hydrogen were taken. The results are fairly good but are not as satisfactory as those obtained with oxygen and air.

acids and removing the carbon dioxide with potassium hydroxide. Duplicate volumetric analyses by absorption with cuprous chloride showed the gas to be 99.7 per cent. pure.

The oxygen which was used in these and the other combustions was made from potassium chlorate and manganese dioxide and was purified by being shaken with a solution of potassium hydroxide. Absorption by alkaline pyrogallol showed it to be very nearly pure, 99.9 per cent.

Two volumes of carbon monoxide unite with one volume of oxygen to form two volumes of carbon dioxide. Hence the volume of the carbon monoxide taken is equal either to the volume of carbon dioxide which is formed, or to twice the contraction resulting from the combustion. In the following tabulation of results the percentages of carbon monoxide obtained in both ways are given. There are also added the percentage results calculated on the assumption that the gas contained only 99.7 per cent. of carbon monoxide as indicated by the absorption with cuprous chloride.

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
	cc.	cc.	cc.	cc.	cc.	cc.	cc.	cc.
bon monoxide taken	73.1	60.7	82.1	80.95	78.1	77.95	83.05	79.0
ygen taken	50.7	49.65	52.2	49.8	50.55	50.8	52.4	50.4
Total	123.8	110.35	134.3	130.75	128.65	128.75	135.45	129.4
idue after combustion	87.4	80.1	93.3	90.4	89.65	89.8	93.95	89.95
traction	36.4	30.25	41.0	40.35	39.0	38.95	41.50	39.45
idue after absorbing CO_2 in OH pipette	14.5	19.5	11.5	9.6	11.7	12.05	11.05	11.25
bon dioxide	72.9	60.6	81.8	80.8	77.95	77.75	82.90	78.70
	Per ct.	Per ct.	Per ct.	Per ct.	Per ct.	Per ct.	Per ct.	Per ct.
, calculated from contraction	99.6	99.7	99.9	99.7	99.9	99.9	99.9	99.9
, calculated from CO_2 formed	99.7	99.8	99.6	99.8	99.8	99.7	99.8	99.6
, from contraction, assuming s to be 99.7 per cent. pure	99.9	100.0	100.2	100.0	100.2	100.2	100.2	100.2
, from CO_2, assuming gas to 99.7 per cent. pure	100.0	100.1	99.9	100.1	100.1	100.0	100.1	99.9

METHANE.

Methane was first prepared from zinc dust and chloroform in aqueous alcohol, as proposed by Sabanejeff[1] and recommended by Phillips.[2] The product was, however, very unsatisfactory as

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[1] *Ber. d. chem. Ges.*, 9, 1810.

[2] *Am. Chem. J.*, 16, 172.

it contained not only vapors of alcohol and chloroform but also a considerable amount of hydrogen. Methane was then made from sodium acetate and soda-lime and the hydrogen which is simultaneously formed was removed by passing the gas over palladium black. Four determinations, by this method, of the hydrogen present gave the following results :

	I.	II.	III.	IV.
	cc.	cc.	cc.	cc.
Gas taken	99.2	100.0	99.55	99.2
Residue after passage over palladium black	92.75	93.5	93.0	92.8
Hydrogen	6.45	6.5	6.55	6.4
	Per cent.	Per cent.	Per cent.	Per ct.
Hydrogen	6.5	6.5	6.6	6.5

It was to be expected that the residue from the hydrogen determinations would be pure methane, but when 40.75 cc. of this gas was burned with oxygen in the combustion pipette the contraction amounted to 81.65 cc. and 42.5 cc. of carbon dioxide was formed, thus plainly indicating the presence of a gas or vapor with more than one carbon atom in the molecule. The gas was therefore not of sufficient purity to give trustworthy data concerning the accuracy of the combustion method when used for methane alone, and unfortunately there was not sufficient time at our disposal to permit of further experiments upon the preparation of pure methane. In order, however, to obtain, in an indirect way at least, some idea as to the accuracy of the method in the determination of methane, a series of combustions was made of the residue from illuminating gas after the removal of the absorbable gases.

SIMULTANEOUS COMBUSTION AND DETERMINATION OF HYDROGEN AND METHANE.

Illuminating gas was passed into fuming sulphuric acid to remove hydrocarbon vapors and heavy hydrocarbons, then shaken with alkaline pyrogallol to remove oxygen, carbon dioxide, and the fumes of the sulphuric acid, and finally shaken first with old and then with fresh cuprous chloride to remove carbon monoxide. Measured portions of the residue which now contained hydrogen, methane, and nitrogen were then introduced into the combustion pipette and burned with oxygen in the manner described above.

	I.	II.	III.	IV.	V.
	cc.	cc.	cc.	cc.	cc.
Gas residue taken	61.4	64.5	67.0	64.0	65.7
Oxygen taken	98.5	96.55	98.55	97.6	100.0
Total	159.9	161.05	165.55	161.6	165.7
Residue after combustion	58.8	54.95	55.3	56.3	57.6
Contraction	101.1	106.1	110.25	105.3	108.1
Residue after absorbing CO_2 in KOH pipette	34.3	29.15	28.6	30.7	31.4
Carbon dioxide found	24.5	25.80	26.7	25.6	26.2
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Hydrogen	56.4	56.3	56.6	56.4	56.5
Methane	39.9	40.0	39.9	40.0	39.9
Nitrogen (diff.)	3.7	3.7	3.5	3.6	3.6

To obtain an idea of the relative accuracy and constancy in the results by the combustion and explosion methods in the hands of the same operator, two analyses of the same gas residue were carefully made with the Hempel explosion pipette, mercury being used here also as the confining liquid.

	I.	II.
	cc.	cc.
Gas residue taken	12.0	12.35
Air added	83.2	83.45
Total	95.2	95.8
Residue after explosion	75.3	75.25
Contraction	19.9	20.55
Residue after absorbing CO_2 in KOH pipette	70.35	70.2
Carbon dioxide found	4.95	5.05
	Per cent.	Per cent.
Hydrogen	55.3	56.4
Methane	41.3	40.9
Nitrogen (diff.)	3.4	2.7

SIMULTANEOUS COMBUSTION AND DETERMINATION OF CARBON MONOXIDE, HYDROGEN, AND METHANE.

A mixture of these gases together with nitrogen was obtained by extracting from illuminating gas by means of the usual absorbents, only the hydrocarbon vapors, heavy hydrocarbons, oxygen, and carbon dioxide. A measured volume of the residue was transferred to the combustion pipette and burned with oxygen. The residual gas was then passed back into the burette, measured to ascertain the contraction, and then passed into the caustic potash pipette to absorb the carbon dioxide and again drawn back and measured. In the meantime a known volume of hydrogen had been brought into the combustion pipette. This was then connected with the burette which now contained nitrogen and the unconsumed oxygen, the current was turned on, and the oxygen was passed over into the hydrogen. From the resulting contraction the excess of oxygen was ascertained and the difference between this and the oxygen first taken gives the amount of oxygen consumed in the combustion of the carbon monoxide, hydrogen, and methane.

Having thus ascertained the contraction resulting from the combustion, the volume of carbon dioxide formed, and the amount of oxygen consumed, we have all the data necessary for the calculation of the amounts of carbon monoxide, hydrogen, methane, and nitrogen existing in the original mixture. The reactions which take place in the combustion and the volume changes due to these reactions are the following :[1]

$$\underset{\text{2 vols.}}{2CO} + \underset{\text{1 vol.}}{O_2} = \underset{\text{2 vols.}}{2CO_2}.$$

Contraction in burning 2 vols. CO = 1 vol.
Hence contraction for 1 vol. CO = $\frac{1}{2}$ vol.

$$\underset{\text{2 vols.}}{2H_2} + \underset{\text{1 vol.}}{O_2} = \underset{\text{liquid.}}{2H_2O}.$$

Contraction in burning 2 vols. H = 3 vols.
Hence contraction for 1 vol. H = 1.5 vols.

$$\underset{\text{1 vol.}}{CH_4} + \underset{\text{2 vols.}}{2O_2} = \underset{\text{1 vol.}}{CO_2} + \underset{\text{liquid.}}{2H_2O}.$$

Contraction in burning 1 vol. CH_4 = 2 vols.

From the above equations we have
Contraction = $\frac{1}{2}$ CO + $\frac{3}{2}$ H + $2CH_4$.
Carbon dioxide formed = CO + CH_4.
Oxygen consumed = $\frac{1}{2}$CO + $\frac{1}{2}$H + $2CH_4$.

From these last three equations a variety of formulas for the calculation of the various components of the original mixture may be derived. Noyes and Shepard give

(1) H = Contraction minus oxygen consumed.
(2) CO = $\frac{2}{3}$($2CO_2$ + $\frac{1}{2}$H—oxygen consumed).
(3) $CH_4 = CO_2 - CO$.

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[1] Cf. Vignon : *Bull. Soc. Chim.*, *1897*, p. 832.

(4) $N = \text{Original volume} - (H + CO + CH_4)$.

Instead of (2) and (3) we may also use

$$CO = CO_2 - CH_4.$$

$$CH_4 = \frac{2\ \text{Contraction} - CO_2 - 3H.}{3}$$

If no nitrogen is present in the original mixture the following equations of Vignon may be employed, V representing the volume of the gas mixture taken for the combustion.

$$H = V - CO_2.$$

$$CO = \tfrac{1}{3}CO_2 + V - \tfrac{2}{3}\ \text{contraction}.$$

$$CH_4 = \tfrac{2}{3}CO_2 + \tfrac{2}{3}\ \text{contraction} - V.$$

	I. cc.	II. cc.	III. cc.	IV. cc.
Volume of gas residue taken	83.45	85.05	83.05	86.95
Oxygen added	97.65	96.25	97.90	99.95
Total	181.10	181.30	180.95	186.90
Volume after combustion	49.3	46.95	49.75	49.5
Contraction resulting from combustion	131.8	134.35	131.20	137.4
Volume after absorption of carbon dioxide	13.05	10.15	13.75	12.0
Volume of carbon dioxide formed in the combustion	36.25	36.80	36.0	37.5
Hydrogen taken for determination of excess of oxygen	50.65	40.8	41.35	40.9
The preceding + volume remaining after absorption CO_2	63.70	50.95	55.10	52.9
Volume after combustion	32.15	28.3	21.2	24.75
Contraction resulting from this combustion	31.55	22.65	33.9	28.15
Oxygen in excess (⅓ preceding contraction)	10.52	7.55	11.3	9.38
Oxygen consumed in combustion of CO, H, and CH_4	87.13	88.70	86.6	90.57

From the above experimental results the calculated percentages of the various gases are as follows :

	I. Per cent.	II. Per cent.	III. Per cent.	IV. Per cent.
Carbon monoxide	6.2	6.1	6.2	6.0
Hydrogen	53.5	53.7	53.7	53.9
Methane	37.3	37.2	37.2	37.1
Nitrogen (difference)	3.0	3.0	2.9	3.0

In carrying on the various combustions by which the above results were obtained, it was observed that a much stronger current is required to maintain the spiral at a red heat in an atmosphere of gases of low molecular weight than is needed with heavier gases, this being probably due to the different thermal capacities of the various gases and to the varying velocities of the different gas molecules. This phenomenon is especially marked in the combustion of hydrogen, for with this gas it is necessary to markedly decrease the strength of the current as the combustion proceeds, since otherwise a current which will heat the spiral only to redness in the atmosphere of hydrogen at the beginning, is liable to melt the platinum wire in the mixture of nitrogen and oxygen which remains after the combustion is completed.

An interesting reaction which was observed during the progress of the work is that a mixture of methane and water vapor when heated by the spiral reacts as follows:

$$CH_4 + H_2O = CO + 3H_2.$$[1]

According to this equation one volume of methane should yield four volumes of the mixture of carbon monoxide and hydrogen. On actual experiment it was found that 24.1 cc. of impure methane expanded to 74.5 cc. from which cuprous chloride absorbed 16.5 cc. This 16.5 cc. of carbon monoxide shows that an equal volume of methane was present in the original gas, and according to the above equation the 16.5 cc. of methane on being heated in the presence of the water vapor, should show an increase in volume of 49.5 cc. The expansion observed was 50.4 cc., a result which is sufficiently close to sustain the above reaction. That the observed expansion does not agree more nearly with the calculated increase in volume is doubtless due to the fact that at high temperatures carbon monoxide reacts with water vapor, forming carbon dioxide and hydrogen.[2] We confirmed the accuracy of this statement by introducing into the combustion pipette 79.75 cc. of pure, moist carbon monoxide, and heating the spiral for five minutes. The volume was thereby increased to 82.75 cc. from which 3.05 cc. of carbon dioxide were absorbed by potassium hydroxide.

CORNELL UNIVERSITY, July, 1898.

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[1] Several years ago Coquillion observed that the same reaction takes place in the presence of a red-hot palladium spiral.—*Compt. rend.*, 86, 1198.

[2] Cf. Dixon: *J. Chem. Soc.*, 49, 99, 100.

THE SURFACE-TENSIONS OF AQUEOUS SOLUTIONS OF ALKALINE CHLORIDES.

BY C. E. LINEBARGER.

Received December 31 1898.

THE object of this investigation is to determine the surface-tensions of aqueous solutions of the chlorides of lithium, sodium, and potassium up to the limits of their solubility. The apparatus described in a previous number of this Journal[1] permits of the same degree of accuracy when the liquid is filled with suspended particles as when it is clear. The saturation of a liquid with a solid can accordingly be accomplished with the capillary tubes right in the mixture, and the surface-tension can be measured from time to time until the saturation is completed. The operations of determining the surface-tension of a saturated solution are as follows: The solution is saturated in a thermostat at the required temperature. A sample is then transferred to the tube of the apparatus and, the temperature being the same as before, several readings are made. Some of the powdered solid is then added and with frequent agitation readings are taken at intervals of thirty minutes or so for several hours. If the preliminary saturation has been total, these readings are the same.

The alkaline chlorides used were bought as chemically pure. Lithium chloride (Koenig's C. P.) was not subjected to further purification, but the chlorides of sodium and potassium were recrystallized a couple of times.

The solutions of potassium and of sodium chloride were prepared by weighing the well-dried salts and dissolving them in known weights of water. The solutions of lithium chloride were

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[1] Vol. 18, No. 6, June, 1896. I have substituted for the compression bulb therein described the following simple arrangement. A large bottle filled with water is placed on a bench on the table so as to give an effective fall of water of about two feet. The water is siphoned over into a second bottle, the siphon-tube reaching to its bottom. This bottle is closed with a twice-perforated rubber stopper, through which pass the siphon-tube and an elbow-tube connected with the capillary tubes of the apparatus. The air forced from the second is passed through a piece of thermometer tubing to prevent too rapid a flow and a solid glass bead placed in the connecting rubber hose to act as a stop-cock. By pressing the hose around the head with the thumb and finger so as to form a channel alongside it, the flow of air can be regulated with great nicety.

made from weighed quantities of water and of a strong solution of the salt that had been analyzed for chlorine.

The specific gravities were determined with pycnometers of different styles and sizes, and are referred to water at 4°. Their accuracy is denoted by the number of decimal places retained.

The data are given in the following tables:

SURFACE-TENSIONS OF AQUEOUS SOLUTIONS OF LITHIUM CHLORIDE.

Temperature = 25°.

Per cent. of salt.	Mols. of salt per liter.	Specific gravity.	Apparatus constant.	Distance between tubes in $\frac{1}{20}$ inch.	Surface-tension in dynes per cm.
9.18	2.28	1.05023	1.259	54.50	73.17
18.06	4.70	1.10298	1.259	55.38	78.17
26.14	7.11	1.15468	1.259	56.50	83.39
40.49	12.02	1.25904	1.259	58.23	93.88

Lithium chloride is so soluble and prone to supersaturation that the surface-tension of its saturated solution was not measured. As a hydrate and not the pure salt crystallizes from its solution, it was not thought that this datum would present anything of especial interest. The strongest solution examined was very near to saturation.

SURFACE-TENSIONS OF AQUEOUS SOLUTIONS OF SODIUM CHLORIDE.

Temperature = 25°.

Per cent. of salt.	Mols. of salt per liter.	Specific gravity.	Apparatus constant.	Distance between tubes in $\frac{1}{20}$ inch.	Surface-tension in dynes per cm.
5.62	1.04	1.0370	2.366	29.29	71.59
10.87	2.06	1.0726	2.366	28.41	73.04
13.52	2.52	1.0944	1.259	52.63	73.71
15.72	3.04	1.1123	2.366	28.11	75.04
		Temperature = 20°.			
5.62	1.04	1.0388	2.366	29.01	72.38
10.87	2.06	1.0746	2.366	28.55	73.78
15.72	3.04	1.1146	2.366	28.30	75.87
26.19[1]	5.38[1]	1.20046	2.333	28.27	80.60

The surface-tension of a sodium chloride solution saturated at 25° was not determined. The determinations at 20° and 25° show such constant differences that its value may be calculated with no appreciable error by subtracting from the surface-tension of the solution saturated at 20° the average difference between

[1] Saturated solution.

the determinations made on the same solutions at the two temperatures, for the solubility of common salt varies very slightly with the temperature.

SURFACE-TENSIONS OF AQUEOUS SOLUTIONS OF POTASSIUM CHLORIDE.

Temperature = 25°.

Per cent. of salt.	Mols. of salt per liter.	Specific gravity.	Apparatus constant.	Distance between tubes in $\frac{1}{50}$ inch.	Surface-tension in dynes per cm.
9.09	1.29	1.0555	1.257	53.45	72.05
10.71	1.53	1.0665	1.278	52.26	72.33
16.67	2.48	1.1069	1.257	52.02	73.61
23.08	3.57	1.1526	1.257	51.11	75.39
26.44[1]	4.18	1.17885	1.257	50.98	76.97

The data given in the preceding tables are plotted in Figs. 1 and 2; the ordinates of both are surface-tensions, and the abscissas concentrations, expressed in the first figure as percentages, and in the second as mols. per liter.

The percentage curves show that the surface-tensions are the greater the smaller the molecular mass of the salt. Thus, the curve for sodium chloride lies about midway between those for lithium and potassium chloride. The surface-tension of these salt solutions is seen to be a function of their molecular masses. This is very plainly brought out by the curve in Fig. 2, where the concentrations are expressed in mols. per liter. It is seen that the surface-tensions of the solutions of the alkaline chlorides are the same, for the curve represents the behavior of each of the salts examined.

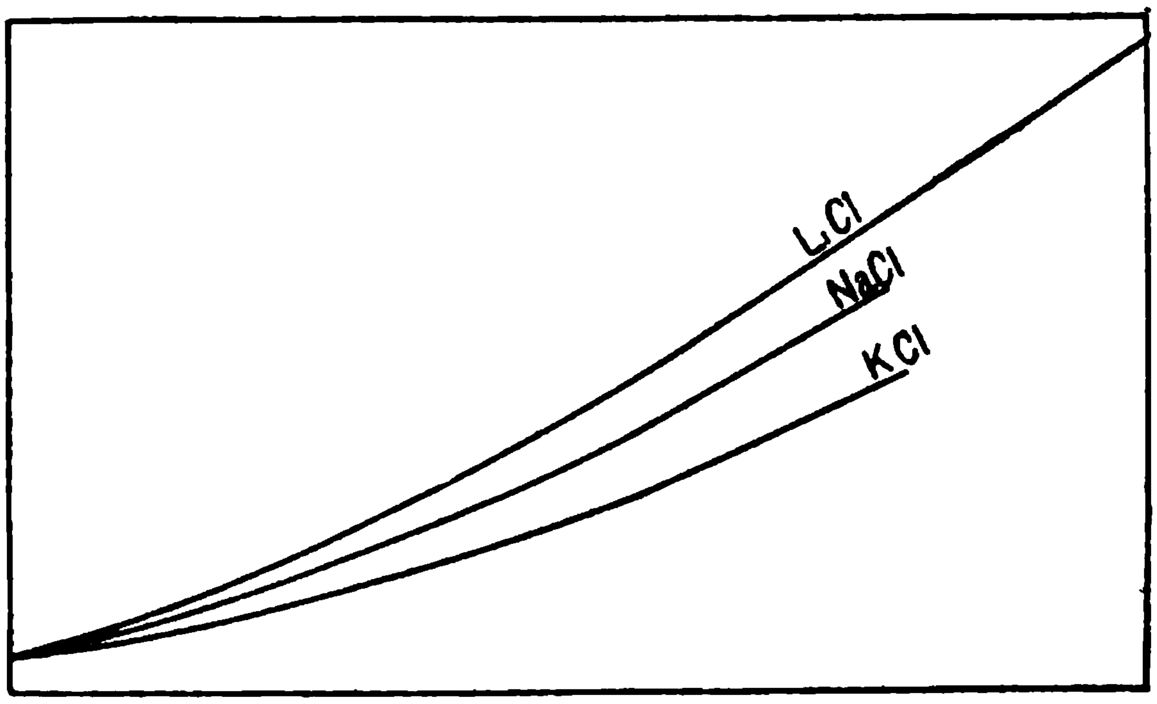

Fig. 1.

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[1] Saturated solution.

As has already been found by Bulinginsk,[1] Valson,[2] Quincke,[3] Volkmann,[4] Rother,[5] Traube,[6] and Dorsey,[7] the surface-tensions of the solutions of the salts increase with the concentration. The investigators named did not use very concentrated solutions, however, and assumed that the surface-tension was a linear function of the concentration. This conclusion is not justified when the surface-tension is measured throughout the entire range of solubility of an alkaline chloride. The curve in Fig. 2 is slightly convex towards the axis of abscissas. It is, however, for small changes in concentration, practically a straight line, and for such concentration changes a formula of the form $\gamma' = \gamma + ka$ may be applied, where γ' denotes the surface-tension of the solution, γ that of water, k a constant, and a the concentration expressed in mols. per liter. At 25° the surface-tension of pure water is 69.85 dynes per cm.[8] We accordingly may establish the following equations :

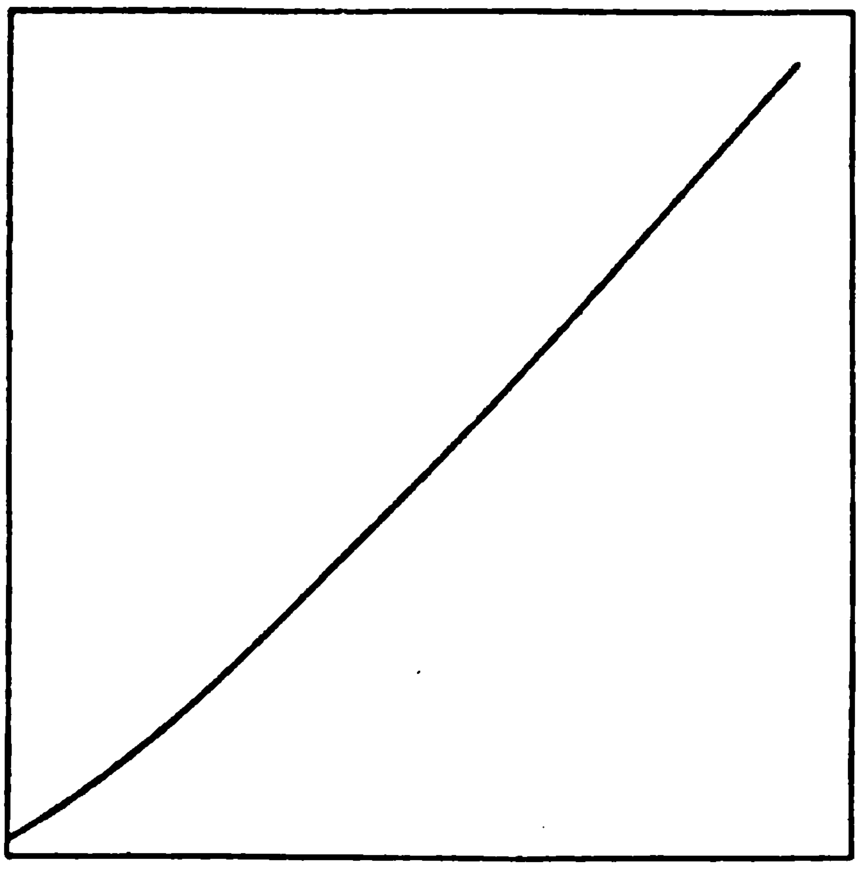

Fig. 2.

Between 0 and 1 mol. $\gamma' = 69.85 + 1.48\,a$,
" 1 " 2 mols. $\gamma' = 69.85 + 1.55\,a$,
" 2 " 3 " $\gamma' = 69.85 + 1.62\,a$,
" 3 " 4 " $\gamma' = 69.85 + 1.70\,a$,
" 4 " 5 " $\gamma' = 69.85 + 1.78\,a$.

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[1] *Pogg. Ann.*, 134, 440 (*1868*).

[2] *Ann. chim. phys.* (4). 20, 361 (*1870*).

[3] *Pogg. Ann.*, 337 and 560 (*1877*).

[4] *Wied. Ann.*, 17, 353 (*1882*).

[5] *Ibid.*, 21, 576 (*1884*).

[6] *J. prakt. Chem.*, 31, 192 (*1885*).

[7] *Phil. Mag.*, *Nov. 1897*, p. 369.

[8] Ramsay and Shields : *Ztschr. phys. Chem.*, 12, 432 (*1893*).

There are too few data to permit of establishing the values of the constant k for concentrations greater than five mols. Still since the values of the "k's" increase by about 0.08 as the concentration increases by one mol., if it be legitimate to assume that this regularity continues, similar formulas may readily be found for greater concentrations.

ESTIMATION OF THE LIME, POTASH, AND PHOSPHORIC ACID IN HAWAIIAN SOILS PROBABLY AVAILABLE FOR THE IMMEDIATE CROP.

BY WALTER MAXWELL.

Received January 11, 1899.

ASPARTIC ACID METHOD.

1. The hypothetic principle of this method rests upon the assumption that the solvents used shall compare with the solvents that operate in the processes of soil disintegration, and plant-food preparation, in the field.[1]

2. The standards of control of this method are the ascertained results of the natural processes of soil decomposition in the field, under the conditions of climate and nature of the soils of the Hawaiian Islands, as indicated by the "results of cropping" and "the composition of the waters of discharge" flowing from the land into the sea.[2]

3. The sample is obtained by the mode given in previous publications; *viz.*, by the pipe, where this is practicable, otherwise by the spade. The calculation of available matter per acre is based upon the specific gravity (weight of the cubic foot) of the soil, and the depth to which the sample is taken. In thin soils the amount is less, in deep soils greater, than the amount found in one acre to a depth of one foot, upon which depth, calculations, so far, in the use of this method, have been based.

4. The solvent used in this method is aspartic acid. This acid was adopted because it was found that "aspartic acid dissolves phosphoric acid, lime, potash, and other bases (iron and alumina) out of the soil in almost the exact proportions that these ele-

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[1] See the author's work on the "Lavas and Soils of the Hawaiian Islands;" also this Journal, 20, 107 (*1898*).

[2] See "Lavas and Soils of the Hawaiian Islands."

tube inserted. The mixture is heated sufficiently in the Bunsen flame to freely volatilize the alcohol which then escapes through the jet and is burned in the flame of a second Bunsen burner. If boric acid is present, the flame will show its characteristic green tint.

In order to determine whether the test made in this manner was any more delicate than by the old method, solutions of known strength were made up, and comparative tests made of the two methods. In each of these tests, the following quantities of the different substances were taken: Borax solution, one cc.; sulphuric acid (sp. gr. 1.84), two cc.; and alcohol, ten cc. By the usual method, it was possible to detect the boric acid in

a solution, one cc. of which contained 0.01 gram of boron trioxide (B_2O_3). With the new apparatus we found that with a solution of one-tenth this strength (one cc. = 0.001 gram boron trioxide), a faint green color was perceptible, thus showing it to be an improvement on the test as usually conducted. Copper and barium salts were subjected to the same test, and it was found they did not interfere, giving no coloration to the flame.

These comparisons completed, we thought it advisable to carry our work still further and determine the degree of sensibility of the other tests in use. The fluoride test was made as follows: A bead of potassium fluoride and acid potassium sulphate was made in the loop of a platinum wire, at as low a heat as possible in order that the acid sulphate might not be decomposed. This bead was then dipped in the borax solution and heated in the Bunsen flame. A solution containing 0.01 gram boron trioxide in one cc. gave a faint green flame. With 0.001 gram per cc. no color was visible.

The glycerine test was also tried, the operation being conducted as follows: A bead of acid potassium sulphate was made and dipped into the borax solution, and then ignited sufficiently to decompose the sulphate and liberate the boric acid. After cooling, it was dipped into glycerine, and the latter ignited in the flame On removing the bead from the flame, the glycerine continues to burn, giving a green flame if any boric acid is present. The limit of sensibility of this method was found to be a solution containing 0.001 gram boron trioxide per cc., this amount giving a faint green tinge to the flame.

Leaving the flame tests we now come to the one with turmeric paper. The solution to be tested was acidified with dilute hydrochloric acid, and the paper moistened with the acidified solution was dried at 100°. A solution containing only 0.0001 gram boron trioxide gave a distinct pink color on the paper, thus proving turmeric to be the most delicate of all.

In comparing the delicacy of the various tests, it is well to remember that the quantity of boric acid actually taking part in the bead and turmeric paper tests, is much less than the amount contained in one cc. of the solution tested. For example in the bead tests, one drop of the solution was sufficient to saturate the bead, and as one cc. was found to contain about fifteen drops the amount of boric acid actually used was only one-fifteenth of that present in one cc. For the tumeric paper test, two drops of the solution were ample.

In the following table the results have been calculated on this basis.

	Limit of test. Gram.	B_2O_3 actually present in test. Gram.	B_2O_3 in solution. Per cent.
Boric ether flame (old method)	0.01	0.01	1.0
Boric ether flame (new method)	0.001	0.001	0.1
Glycerine method	0.001	0.00006	0.1
Potassium fluoride and acid potassium sulphate method	0.01	0.0006	1.0
Turmeric paper method	0.0001	0.000013	0.01

Although the test with turmeric paper is by far the most delicate, it is a well-known fact that with the average student in qualitative analysis, the results are very uncertain; should a trifle too much acid be used to liberate the boric acid, the turmeric paper when dried will be brown instead of pink. If insufficient acid be added, there will be no boric acid coloration of the paper, even though considerable borate may be present.

The method that we recommend is intended to supplant the usual watch-glass or porcelain dish method that is in general use in most qualitative laboratories. Our modification of this method not only makes the test more delicate, but may be performed with the simplest apparatus; a test-tube, cork, and small piece of tubing are all that is necessary.

THE SPECIFIC GRAVITY OF CESIUM.

BY A. E. MENKE.

Received January 30, 1899.

THE specific gravity of cesium was determined many years ago by Setteler and given as 1.88. He, however, worked with relatively small quantities of the metal (0.6 and 1.1 gram) as his method of preparation did not allow him to obtain cesium in quantity. I have recently, in collaboration with Prof. Hugo Erdmann of Halle, made cesium on a large scale and it seemed to me advisable to redetermine the specific gravity.

The cesium for this purpose was purified by several redistillations in hydrogen, and then examined spectroscopically. The metal was weighed in hydrogen and then under liquid paraffin giving the following results as the specific gravity referred to water.

No. 1	2.4001
No. 2	2.4004
No. 3	2.3996
No. 4	2.4002
No. 5	2.3998
No. 6	2.4001
Mean	2.40003

In each case not less than four grams of metal were employed, and the proper correction made for hydrogen weighing.

These results change the atomic volume of cesium from the figure usually given (70.6 to 55.3) which does not make the drop in the atomic volume curve from cesium to barium as abrupt as heretofore. It however affects the symmetry of the vertical column. The specific gravity of rubidium is probably not correct. I expect to redetermine it shortly.

The following parts of the atomic volume tables illustrate the points in question:

TABLE OF ATOMIC VOLUMES WITH SP. GR. OF CESIUM 1.88.

K......	45.4	Ca......	25.4	Sc......	17
Rb	56.2	Sr......	35	Y	24.8
Cs	70.6	Ba	36.5	La	22

TABLE OF ATOMIC VOLUMES WITH SP. GR. OF CESIUM 2.40003.

K......	45.4	Ca......	25.4	Sc......	17
Rb	56.2	Sr......	35	Y	24.8
Cs	55.3	Ba	36.5	La	22

These experiments confirm Beketoff's results on the atomic volume of cesium.

UNIVERSITY OF BERLIN.

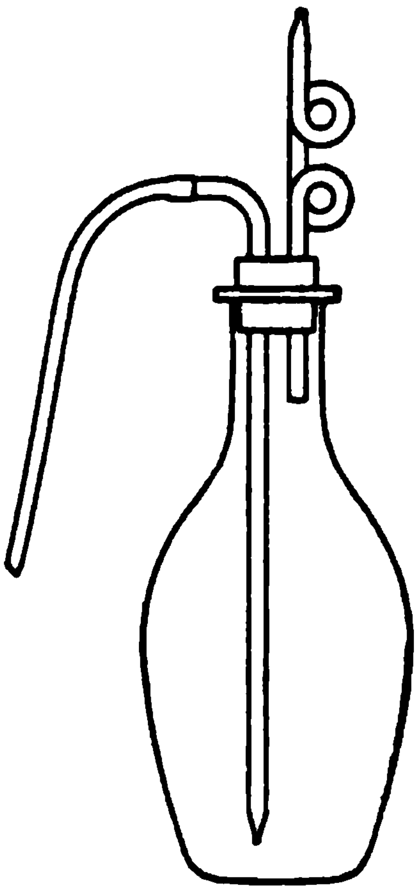
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF LAFAYETTE COLLEGE.]

AN APPARATUS TO FACILITATE HYDROGEN SULPHIDE PRECIPITATIONS.

BY RICHARD K. MEADE.

Received January 21, 1899.

THE piece of apparatus described below has been in use here for the past term by the students of my class in qualitative analysis and answers fully the purpose for which it was designed: to hasten the precipitation of the copper-arsenic group by hydrogen sulphide. It consists of an ordinary flask or gas bottle of any suitable form and capacity, provided with a closely-fitting two-hole rubber stopper. A piece of glass tubing bent at right angles passes through one hole to the bottom of the flask, serving as an inlet for the gas. This is connected with the hydrogen sulphide generator by a half or three quarters of a yard of light rubber tubing. A piece of glass tubing bent in the gas flame to the form shown in the cut passes through the other hole and serves as an outlet for the gas.



The solution to be precipitated is poured into the flask, this in turn corked up, and the apparatus stood in the hood. The gas is now passed into the solution and the flask violently shaken by hand. The bends in the exit tube keep any of the solution from being thrown out of the flask. The churning up of the solution with the hydrogen sulphide gas quickly throws out of solutions the metals of the copper-arsenic group.

The young men tell me that not only is the time necessary for complete precipitation greatly shortened but the sulphides are obtained in a form more easily filtered and washed, by the use of this apparatus.

EASTON, PA., January 19, 1899.

ACTION OF A HARD WATER ON CERTAIN METALS.

BY JAS. LEWIS HOWE AND J. L. MORRISON.

Received February 25, 1899.

THE work described in this paper was undertaken for the purpose of studying the action of the town water supply of Lexington, Va., on brass, as complaint had been made by plumbers and others that brass faucets, valves, etc., were rapidly corroded by the water and rendered useless.

An analysis of the water furnished me by Col. N. B. Tucker, of the Virginia Military Institute, is as follows .

	Parts per 100,000.
Lime	7.30
Magnesia	4.065
Ferrous oxide	0.2057
Soda	0.3608
Carbon dioxide	30.196
Sulphur trioxide	0.2127
Silica	0.730
Chlorine	trace
Potash	absent

The relatively high proportion of magnesia is due to the fact that most of the limestone of the region is highly magnesian. Several different metals were tested and in each case a duplicate was made with distilled water. The method used was as follows: The metals were in thin strips except the brass which was in the form of wire. The surface was thoroughly cleaned with emery paper, the metal weighed, and the area of exposed surface measured. With each metal two bottles of about a half-liter capacity and two open jars holding about two liters were used. One of the bottles was filled with town water and the other with distilled water and tightly corked, care being taken that no air should be in the bottle. One jar was filled with town water, the other with distilled water and left open to the air with a slight protection from dust. As the water evaporated more water was added. The temperature ranged from 10° to 20°, or occasionally perhaps 25°. After four months the metals were removed, and, after brushing off any loosely adhering deposit, weighed. The water was tested qualitatively for the presence of the metal in solution. The amounts of metal used in each case and the surface were approximately as follows: Brass, 36 grams, 105 sq. cm.; zinc, 56 grams, 170 sq. cm.; copper, 17 grams, 243 sq. cm.; iron, 64 grams, 391 sq. cm.; lead, 375 grams, 500 sq. cm.; aluminum (thin commercial sheet), 1.6 grams, 175 sq. cm.

In a further experiment a bundle of brass wire was packed in the pipes behind two of the laboratory faucets. One of these faucets (A) was used almost constantly all day, the other (B) perhaps half as much. These wires weighed respectively 36.540 and 36.527 grams and presented each 105.5 sq. cm. surface; these were left in position three and one-half months.

The results are expressed in the following table in terms of milligrams per square centimeter of surface:

BRASS.

	Loss or gain in weight.	
Town water, closed bottle,	0	Surface bright; no copper or zinc in water.
" " open jar,	0.047 loss	Surface bright, except at ends of wires; no copper but much zinc in water.
Distilled water, closed bottle,	0	Surface bright; no copper or zinc in water.
" " open jar,	0.019 gain	Surface bright except at ends of wires; no copper or zinc in water.
Faucet A,	3.742 loss	Surface showed much tarnish
" B,	1.108 "	Surface showed much tarnish

	Loss or gain in weight.	
	ZINC.	
Town water, closed bottle,	1.54 gain	Surface slightly oxidized; zinc in water.
" " open jar,	2.523 "	Surface much oxidized; much zinc in water.
Distilled water, closed bottle,	0.348 "	Surface slightly oxidized; trace of zinc in water.
" " open jar,	0.1165 "	Surface slightly oxidized; trace of zinc in water.
	COPPER.	
Town water, closed bottle,	0	Surface bright; slight trace of copper in water.
" " open jar,	0.16 loss	Surface tarnished, copper in water.
Distilled water, closed bottle,	0	Surface bright; trace of copper in water.
" " open jar,	0.131 gain	Surface tarnished, red to black; copper in water.
	IRON.	
Town water, closed bottle,	0.025 loss	Surface slightly rusted; iron in water; 0.15 gram deposit.
" " open jar,	6.966 "	Much rust; iron in water; 4.575 gram deposit.
Distilled water, closed bottle,	0.077 "	Surface tarnished; iron in water; 0.085 gram deposit.
" " open jar,	7.086 "	Much rust; iron in water; 4.965 grams deposit.
	LEAD.	
Town water, closed bottle,	1.304 loss	Surface bright; lead in water.
" " open jar,	1.152 "	Surface somewhat tarnished; little lead in water.
Distilled water, closed bottle,	2.306 "	Surface bright; lead in water.
" " open jar,	3.391 "	Surface much tarnished; much lead in water.
	ALUMINUM.	
Town water, closed bottle,	0	Surface bright; no aluminum in water.
" " open jar,	0	Surface bright; no aluminum in water.
Distilled water, closed bottle,	0	Surface bright; no aluminum in water.
" " open jar,	0.128 loss	Surface much tarnished; aluminum in water.

This table reveals several points regarding the action on metals of a hard water containing an excess of carbon dioxide with considerable magnesia, and little sulphate and no chlorine.

1. Such a water acts readily upon zinc, far more readily than does distilled water, and it seems to be able to dissolve out the zinc in brass, leaving the brass much corroded. This would explain the action of the water on brass faucets, etc., above mentioned. Such a water should not be conveyed through zinc-lined iron pipes.

2. The hardness of such a water is no protection against its action on lead, this water having more than half as much action as distilled water when protected from the air.

3. Protected from the air, the action upon iron is comparatively slight.

4. Aluminum is perfectly resistant against a water of this character.

Similar experiments were carried out with nickel, but in no case did the water have any action upon it.

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NOTES ON THE ANALYSIS OF DYNAMITE AND GELATINE-DYNAMITE.

BY F. W. SMITH.

Received January 19, 1899.

I.

THE analysis of dynamite is not often described in text-books and the following notes, gleaned from some years' experience, may be of interest to those who have occasion to investigate such products.

A simple case is that of a dynamite containing nitroglycerine, sodium nitrate, wood-pulp, and basic magnesium carbonate or kieselguhr. The following process of analysis is recommended as giving satisfactory results. Weigh out ten grams on a pair of watch-glasses, place in a desiccator over sulphuric acid and leave for at least five days. The loss in weight is called moisture. Weigh about the same amount into a Gooch crucible and extract with pure ether. A drop of the ether is allowed to evaporate on a piece of tissue paper from time to time, and the extraction continued until the paper no longer tastes of nitroglycerine. Dry the residue in an air-bath at about 80° C. for two to three hours and weigh. The loss minus the moisture is called nitroglycerine. In the case of powders containing only nitroglycerine and kieselguhr, this extraction is considerably more difficult, and it is advisable to remove the dynamite from the Gooch crucible to a small beaker and stir up with ether, washing the residue back when free from nitroglycerine. After extracting the nitroglycerine, the niter is extracted with cold water, and after the water ceases to extract anything it is displaced by acetone with the object of drying the residue without affecting the starch if any be present. The loss in weight is called sodium nitrate, potassium nitrate being very rarely used. The residue from the water extraction is ignited until free from carbon. The loss is wood-pulp, flour, bran, etc. I have found no satisfactory method for separating these, and rely on testing with iodine for the presence of starch as an indication of the presence of flour, etc.

If no earthy absorbents have been used, the ash after ignition is not likely to be over one-tenth per cent. of the whole sample. If the ash is considerable it is extracted with hydrochloric acid and the residue dried. The loss, expressed in percentages, is subtracted from the percentage of loss on ignition. The loss on ignition minus the loss on extraction with hydrochloric acid is called wood-pulp, etc., while twice the latter is entered as basic magnesium carbonate. This method saves a quantitative determination of the magnesia in the extract and rests on the fact that the basic magnesium carbonate employed as an absorbent loses practically one-half its weight on ignition. The extract should, however, be examined for lime, etc.; a small amount of iron may come from the kieselguhr. If any residue be left after extracting with hydrochloric acid it is examined under the microscope for kieselguhr, mica, etc., or it may be a small amount of venetian red used for coloring the powder.

The following analysis will serve to illustrate the methods:

No. 515.	Per cent.	Per cent.
Moisture	1.3	....
Nitroglycerine	39.6	39.6
Sodium nitrate	46.8	47.1
Wood-pulp	9.5	....
Basic magnesium carbonate	1.8	....
Kieselguhr	1.0	....
	100.0	

The loss on ignition was 10.40 per cent. and on extraction with hydrochloric acid 0.90 per cent. A quantitative determination of the magnesia, calculated as $Mg(OH)_2.3MgCO_3.3H_2O$, gave one and eight-tenths per cent. The portion used for moisture determination may be used to check the extractions.

Lunge's nitrometer may be used to advantage as a check on the analysis. About one-half gram of the dynamite is weighed into a small weighing bottle and about ten cc. of pure sulphuric acid poured over it. It is then allowed to stand from twelve to eighteen hours. In this time the whole usually goes into solution. In the cold the reaction is perfectly calm and no nitrogen is lost. It is then introduced into the nitrometer and decomposed as usual. The result is most conveniently expressed in cubic centimeters of nitric oxide per gram. On the sample mentioned above three determinations in the nitrometer gave: 237.0, 234.5, and 236.5 cc. of nitric oxide per gram. 39.6 per cent. of nitroglycerine gave 116.9 cc., 46.8 per cent. of sodium nitrate gave 122.9 cc. of nitric oxide per gram respectively, total 239.8 cc. The sodium nitrate used is generally ninety-six to ninety-eight per cent. pure; assuming ninety-seven per cent., reduces the calculated cubic centimeters to 236.1. The nitrometer work shows that in this case the ether-soluble portion contains nothing but nitroglycerine, the water-soluble portion nothing but sodium nitrate and its usual slight impurities. Eight minutes agitation in the nitrometer is sufficient for almost all cases.

II. GELATINE-DYNAMITE.

The gelatine-dynamites are considerably more difficult to analyze. The following analysis may be selected as typical:

No. 478.	Per cent.
Moisture	0.4
Nitroglycerine	33.7
Sulphur	1.9
Resin	7.0
Sodium nitrate	54.0
Guncotton	1.1
Wood-pulp	1.9
	100.0

The sample for moisture is weighed out as before. A filter cone (C. S. & S.) is dried and weighed in a weighing bottle and about fifteen grams of the powder weighed into it. This is extracted in a Soxhlet apparatus with chloroform. The loss includes nitroglycerine, sulphur and resin. Sometimes the powder melts together in the hot chloroform, and in that case it must be taken from the filter and broken up in a beaker with cold chloroform until the bulk of the nitroglycerine is dissolved. After extracting with chloroform the residue is extracted with cold water to remove the sodium nitrate, dried and weighed, then extracted with acetone and the loss on extraction with acetone called guncotton. The still remaining portion consists of wood-pulp and earthy absorbents which are treated as above described. Sodium nitrate is appreciably soluble in acetone and should, on that account, be removed before the guncotton. It is often recommended to extract with acetone first and precipitate the guncotton with chloroform. This method gives results which are too high because the sodium nitrate dissolved by the acetone is also precipitated along with the guncotton. Allowance for this can, however, be made by incinerating the guncotton and calculating the ash as sodium nitrate. The second and following extractions can conveniently be made in the filter cone, setting it in a test-tube with perforated bottom. The filter is finally incinerated in a platinum dish with the residue, allowance being made for its ash content which in one case was 11.4 milligrams.

The chloroform solution is evaporated almost to complete absence of chloroform and taken up with glacial acetic acid. The precipitated sulphur is washed into a weighed Gooch crucible and washed further with a little strong alcohol to remove the resin. The nitroglycerine is determined by weighing a suitable portion of the powder (in this case one and two-tenths grams) into a small beaker. Ether is then poured on, and the powder worked over with a platinum spatula. The ether is several times renewed, being poured on a filter and collected in a glass evaporating dish. The ethereal solution is allowed to evaporate spontaneously in a cool place, the dish being covered with tissue paper. After twelve hours the residue can be washed into the nitrometer with acetic acid, care being taken not to use too much acetic acid which retards the reaction of decomposition, while if too little be used the reaction may be extremely violent. Even with the greatest care in evaporation some nitroglycerine is lost and the results are usually about one per cent. low.

The calculated cubic centimeters of nitric oxide per gram on this analysis, assuming the guncotton to contain 11.9 per cent. of nitrogen, are 99.5 for the nitroglycerine, 141.7 for the sodium nitrate, and two and one-tenth for the guncotton; total 243.3. Two determinations in the nitrometer gave 243.8 and 242.7. As the sodium nitrate was certainly not pure, this result shows that the figure entered for nitroglycerine must be too low. Assuming the sodium nitrate to be ninety-eight per cent. pure gives 138.9 cc. and this, plus 2.10 cc. for the guncotton, subtracted from 243.2, total by analysis, gives 102.2 cc. for the nitroglycerine, corresponding to 34.6 per cent. Of course if necessary the water-soluble portion could be isolated and estimated in the nitrometer. The amount given in the analysis, 33.7 per cent., was determined by analyzing the ether-soluble portion in the nitrometer and calculating the nitric oxide obtained as $C_3H_5N_3O_9$. The resin in this case was recognized by its odor, and estimated by difference. An attempt to determine it in alcoholic solution, in presence of nitroglycerine, by titration with alcoholic potash, failed because nitroglycerine by itself is decomposed by alcoholic potash, decolorizing phenolphthalein solution. Some so-called flameless dynamites contain ammonium nitrate. The ammonia is estimated by distillation from aqueous solution and calculated as nitrate.

The two examples given cover the great bulk of dynamites and gelatine-dynamites used in the United States but many other mixtures, often of a very fanciful nature, are occasionally encountered, some of them exceedingly difficult if not impossible to analyze. The methods of analysis given in Guttmann's Manufacture of Explosives, Vol. II, are mainly reliable as far as they go, while some of Sanford's methods are likely to lead to disappointment. His separation of nitroglycerine from camphor is especially difficult to understand since nitroglycerine and carbon disulphide mix completely on the addition of camphor.

It is hoped that this paper will provoke discussion which may lead to the adoption of uniform methods of analysis by the chemists who have to deal with this class of products.

III. VARIOUS NOTES.

The nitrometer is conveniently set by the use of pure potassium nitrate. Exactly one-half gram is weighed into a weighing bottle, covered with sulphuric acid and allowed to stand until the solution becomes clear. The nitric oxide from this is brought into the measuring tube, and the amount of air in the reduction tube, which should also contain a few drops of water, is varied until the gas in the measuring tube shows 110.5 cc. with the air in the reduction tube at 100 cc. The use of potassium nitrate eliminates a large number of errors, such as those of reading the barometers, thermometers, etc. The potassium nitrate may be purified by dissolving it in the least possible quantity of cold water and precipitating with an equal volume of pure alcohol. Three times is generally sufficient, and the absence of chlorides and sulphates may be taken as a criterion of purity. Sodium nitrate, made by dissolving sodium in alcohol and neutralizing with dilute pure nitric acid, may be used as a check on the potassium nitrate. Leaky stop-cocks are a frequent source of annoyance in working with the nitrometer. The stop-cock of the measuring tube may be tested each time by allowing it to stay open for an instant after connecting it to the decomposing bulb by means of a thick-walled rubber tube and allowing the mercury reservoir to be at its lowest position. The mercury should not sink in the measuring tube. This assures the tightness of everything from the lower side of the stop-cock in the measuring tube to the upper side of the stop-cock in the decomposing bulb. The stop-cock in the decomposing bulb may be tested by analyzing the standard potassium nitrate, first with the level of the mercury in the reservoir about six inches above that in the decomposing bulb, and secondly about six inches below. If the first analysis shows too low a result, and the second too high, it points conclusively to a leak. A person having much nitrometer work to do must familiarize himself with the grinding of stop-cocks as they rarely leave the manufacturers' hands in a perfect condition. Grease for the stop-cocks is made from vaseline with the addition of Japan wax and rosin, the proportions being varied in summer and winter to get a product of suitable hardness and consistency.

The refraction method for the valuation of Chili niter gives results from one to one and one-half per cent. higher than those obtained by using the nitrometer and calculating the nitric oxide obtained as sodium nitrate. This is due to the almost unvarying presence of potassium nitrate, and the occasional presence of potassium perchlorate. The latter may be determined by fusing at a low temperature in the presence of powdered cupric oxide. The increase of chlorides after fusion is calculated as potassium perchlorate. The following is a complete analysis of one sample:

No. 471.	Per cent.
Moisture	2.2
Insoluble	0.1
Magnesium sulphate	0.2
Magnesium chloride	0.1
Sodium chloride	0.4
Potassium nitrate	3.6
Sodium nitrate	93.4
Potassium perchlorate	0.0
	100.0

The refraction method gave 96.8 per cent. of sodium nitrate by difference.

THE CALIFORNIA POWDER WORKS,
PINOLE, CONTRA COSTA COUNTY,
CALIFORNIA, January, 1899.

A MODIFICATION OF PIERCE'S METHOD FOR THE DETERMINATION OF ARSENIC IN ORES.

BY J. F. BENNETT, JR.

Received February 20, 1899.

THERE are several methods for the estimation of arsenic in ores in current use, many of which, however, are defective or do not approach the accuracy required even in technical work.

Pierce's method[1] (one of the best of those in general use), with or without Canby's modification, on account of its simplicity, is largely employed in metallurgical works notwithstanding the fact that it is subject to a range of inaccuracy which renders it inadmissible where accurate results are required, and which can be reduced to a minimum only by the most careful execution.

It is my purpose, after having pointed out the defective points

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[1] Proceedings of the Colorado Scientific Society, Vol. I.

in the above method, to present what is thought to be an improvement upon it, intended especially for the determination of arsenic in ores, together with the results of a number of experiments carried on with a view to determining its accuracy.

Pierce, after getting the arsenic into solution as an alkaline arsenate, expels carbonic acid by boiling with an excess of nitric acid and then very carefully neutralizes with ammonia and nitric acid, using litmus paper as an indicator. By Canby's modification the neutralization is effected by means of an emulsion of zinc oxide.

As to the first method, I have found it practically impossible, after making a large number of determinations, to secure concordant results, especially on high grade ores. This is due to the fact that the silver arsenate is highly soluble in a slight excess of either acid or alkali, and slightly soluble in an aqueous solution of ammonium nitrate; while the precipitate under the conditions that exist here, even after vigorous stirring, invariably passes through the filter. I believe it is practically impossible to secure a neutral solution by means of the above reagents and indicator. Litmus paper, as is well known, is not a good indicator under the conditions as they exist above and I have found it entirely inadequate for the purpose of securing the degree of neutralization which is here absolutely indispensable.

Canby's method is little better in this respect, as the neutralization is only partly effected, the acid becoming too weak to attack the oxide but remaining sufficiently strong to dissolve the arsenate. The method which I propose for eliminating the defective points as above mentioned, is based on the following considerations:

(1). "The addition of sodium acetate to a mixed solution of arsenic and nitric acid is sufficient to insure the immediate precipitation of silver arsenate when silver ammonio-nitrate is introduced."[1] Also, silver arsenate is only "more freely soluble in acetic acid than in solution of ammonium nitrate."[2]

(2). The use of phenolphthalein as indicator instead of litmus paper.

(3). The precipitation, as herewith proposed, renders the precipitate granular and as easily filtered as silver chloride.

[1] Kvery, in Crooke's "Select Methods," page 420.

[2] Graham, in Storer's Dictionary of Chemical Solubilities.

Under consideration (1), the precipitation might be effected in a nitric acid solution, but in order to eliminate any solvent action which the presence of nitric acid might have, the precipitation is effected in a sodium acetate solution slightly acid with acetic acid, as will be seen in the scheme which follows: The absence of ammonia salts, etc., permits the use of phenolphthalein as indicator, thereby securing the neutralization promptly and without the tedious delay due to the slow action of the litmus paper. It will be noticed that I state above on the authority of Graham, that silver arsenate is somewhat more soluble in acetic acid than in ammonium nitrate, while I precipitate in acetic acid solution. I will say, however, that the above is a fairly strong solution of acetic acid, while my solution contains only a sufficient excess of acetic acid to destroy the color of the phenolphthalein (a drop or two of dilute acetic acid in 100 cc. of solution), in which I have found the silver arsenate to be practically insoluble.

The method is as follows:

One-half gram of the finely powdered ore is mixed in a large porcelain crucible with from six to ten times its weight of a mixture of equal parts of sodium carbonate and potassium nitrate, preferably by mixing the ore with about two-thirds of the flux and using the balance as a cover. The mass is then heated gradually to complete fusion and kept so for a few minutes, cooled, and the soluble portion extracted with boiling hot water and filtered from the insoluble residue. The arsenic is in the filtrate as alkaline arsenate. Acidify filtrate strongly with acetic acid, cover and boil rapidly for a few minutes to expel carbonic acid; cool, add a few drops of a solution of phenolphthalein in alcohol, then a strong solution of sodium hydroxide to alkaline reaction; then one or two drops of acetic acid which will discharge the purple-red color if too much of the alkali has not been used. The solution should now consist of about 100 cc. Add, in slight excess, while violently agitating with a stirring rod, a neutral solution of silver nitrate, and allow to settle a few minutes, keeping out of direct sunlight. Pour the clear supernatant liquid through the filter, retaining the precipitate in the beaker, and wash once or twice by decantation with cold water. Finally throw the precipitate on the filter and wash thoroughly with cold water. Now place the beaker in which the precipitation was made, under the funnel, fill the funnel full of water, and add twenty cc. strong nitric acid. When the filtrate has run through, wash filter thoroughly three or four times with cold water, make the filtrate up to about 100 cc., and titrate with a standard solution of potassium thiocyanate, according to Volhard;[1] or the silver may be determined by scorifying the filter and precipitate and cupelling. The former method must be adopted in the presence of chlorides.

Following are a few of a large number of determinations made to test the accuracy of this method:

Two hundred and fifty milligrams impure arsenic trisulphide (As_2S_3) were fused as above and the solution made up to 500 cc. Several portions of fifty cc., each containing 0.025 gram impure arsenic trisulphide, were taken and each portion treated as a separate determination from the point at which the filtrate is acidified strongly with acetic acid; then scorified and cupelled. Results are as follows:

TABLE 1.

No. of determination.	Weight of silver button. Gram.	Calculated amount of arsenic trisulphide found. Gram.
1	0.063915	0.02424
2	0.063240	0.02400
3	0.064720	0.02457
4	0.063450	0.02409
5	0.065075	0.02470
6	0.063675	0.02407

One-half gram impure arsenic trisulphide was fused and made up to 500 cc., and portions of 25 cc., containing 0.025 gram of arsenic trisulphide, were treated as above, except that the precipitate was dissolved in nitric acid and titrated with potassium thiocyanate (1 cc. = 0.02875 gram arsenic trisulphide) instead of scorifying and cupelling. Results are as follows:

TABLE 2.

No. of determination.	Standard solution of potassium thiocyanate. cc.	Arsenic trisulphide found. Gram.
1	8.6	0.024725
2	8.6	0.024725
3	8.3	0.023863
4	8.6	0.024725
5	8.6	0.024725
6	8.7	0.025013

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[1] *Ann Chem.* (Liebig), 190, 1.

It will be noticed that the first table gave uniformly low results. This was attributed to the loss of silver in scorification and cupellation, and in order to correct this loss four assays were run containing 0.06512 gram pure silver each, corresponding to 0.024725 gram arsenic trisulphide (the amount found by titration in numbers 1, 2, 4, and 5 in Table 2). The average loss was found to be 0.001 gram silver, which, added to the amounts in Table 1, gave an average result agreeing very closely with those of the above numbers in Table 2.

Following is Table 1 corrected for loss of silver in scorification and cupellation:

TABLE 3.

No. of determination.	Silver found as per Table 1. Gram.	Silver after correction. Gram.	Calculated amount of arsenic trisulphide. Gram.
1	0.063915	0.064915	0.024648
2	0.06324	0.06424	0.024392
3	0.06472	0.06572	0.024954
4	0.06345	0.06445	0.024472
5	0.065075	0.066075	0.025089
6	0.063675	0.064675	0.024457

Average amount of arsenic trisulphide 0.024670

One gram of leucopyrite was fused and made up to 500 cc. Portions of fifty cc. were treated as above and titrated with potassium thiocyanate (1 cc. = 0.0017536 gram arsenic). Results were as follows:

TABLE 4.

No. of determination.	Standard solution of potassium thiocyanate. cc.	Arsenic found. Gram.	Arsenic in ore. Per cent.
1	7.0	0.012275	12.275
2	7.0	0.012275	12.275
3	7.0	0.012275	12.275
4	7.0	0.012275	12.275

LABORATORY AGRICULTURAL COLLEGE OF NEW
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A SIMPLE VOLUMENOMETER.

BY C. E. LINEBARGER.

Received February 14, 1899.

McKENNA[1] has recently described a "New Apparatus for the Determination of Volume," which resembles in several respects one which I have devised and have been using

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[1] This Journal, 21, 50 (1899).

for some time past. While in accuracy and ease of manipulation my apparatus possibly does not surpass McKenna's, it has the advantage of being readily constructed out of pieces of apparatus found in almost any laboratory, and also allows a very easy recovery of the solid whose volume has been determined.

A wide-mouthed bottle (two-ounce) is fitted with a twice-perforated rubber stopper or cork, if the liquid used attacks rubber. Through one of the holes is passed a ten cc. pipette, graduated in tenths of a cc. and permitting of the estimation of $\frac{1}{100}$ cc. Through the other hole passes a funnel tube with a short stem bearing a mark just below the widened part. The stem-end must be flush with the lower surface of the stopper so that the bottle may be completely filled with liquid without imprisoning any air-bubbles. A long piece of rubber tubing is attached to the upper end of the stem and provided with a good pinch-cock of any sort.

To use the apparatus, it is filled with liquid to a little above the stopper, great care being taken to remove all air bubbles. Suction is then applied to the extremity of the rubber tube so as to bring the level of the liquid in the funnel stem to the mark, when the cock is closed. The position of the liquid in the pipette is then noted, the hundredths of cubic centimeters being estimated. A weighed amount of the solid whose volume is to be determined is then placed in the funnel, and the liquid blown up and down gently until the solid is all washed into the bottle. The liquid is then brought to the mark on the funnel stem and the new position of the meniscus in the pipette read off. It is of course advisable to make several adjustments and readings of the levels and take their average.

To eliminate inaccuracy from change of the temperature of the liquid, the bottle may be packed in a box with some non-conducting material, as cotton-wool, etc. This seems to be a needless refinement, however, for the temperature of a laboratory changes but little during the time required for a determination, and it is not necessary to handle the bottle, so that it does not receive heat in that way. Moreover, the error is small compared with the error due to air adhering to the particles of the solid.

To show what results may be obtained with the apparatus, full data are given for a series of determinations made with Ceylon graphite using kerosene as the liquid. The graphite was mostly in the form of a very fine powder, although many pieces as large as a grain of wheat were present. The kerosene had been dried by standing for three years over sodium shavings. The temperature of the liquid (about 20°) did not change by 0.5° during the experiments. Ten grams of the graphite were added each time.

READINGS ON PIPETTE.

Before solid was added. cc.	After solid was added.	After ten grams more solid was added.
9.92	5.67	1.42
9.90	5.67	1.44
9.91	5.64	1.43
9.91	5.66	1.43

Volume of ten grams of graphite ·········
$$\begin{cases} 9.91-5.66=4.25 \\ 5.66-1.43=4.23 \end{cases}$$

Density of graphite ·····················
$$\begin{cases} \dfrac{10.00}{4.15}=2.35 \\ \dfrac{10.00}{4.23}=2.36 \end{cases}$$

The apparatus was taken apart, cleaned, dried and reassembled, and two more determinations made. The volumes found were 4.22 and 4.26, respectively, and the corresponding densities 2.37 and 2.34.

Of course, other dimensions than those given above for the apparatus may be taken. Also, if it is desirable to know the temperature exactly, a thermometer may be introduced directly into the liquid by using a three-hole stopper.

THE SOLUBILITY, IN WATER, OF CERTAIN NATURAL SILICATES.

BY GEORGE STEIGER.

Received February 11, 1899.

IN this Journal for October, 1898, there is a preliminary paper upon this subject by Professor F. W. Clarke. The results shown in that paper were of such a character, that it was thought worth while to carry the investigation further, and an attempt has been made to show in what degree the different minerals are attacked by water after long standing.

The work was carried out as follows: One-half gram of each of the finely ground minerals was weighed out, and placed in a two ounce bottle with fifty cc. of water. These bottles were set aside where the temperature remained about 70° F. for one month, and were shaken from time to time. At the end of the period all were filtered, and the solutions were titrated with a standard hydrochloric acid solution, methyl-orange being used for an indicator.

What has gone into solution by this treatment I cannot say, sometimes soda, sometimes potash, possibly sometimes lime, but for the sake of comparison the results in the following table have been calculated in terms of Na_2O; although the percentage of sodium is very small in some of the specimens. I have given also in another column, the percentage of the combined alkalies as shown by analysis of specimens from the same localities.

	Formula.	Per cent. of combined alkalies by analysis.	Equivalent of Na_2O in solution.
Pectolite, Bergen Hill, N. J....	$Ca_2(SiO_3)_3NaH$	9.11	0.57
Muscovite....................	$Al_3(SiO_4)_3KH_2$	10.00	0.32
Natrolite, New Jersey..........	$Al_2(SiO_4)_3Na_2H_4$	15.79	0.30
Lintonite, Lake Superior......	$Al_6(SiO_4)_6(CaNa_2)_3.7H_2O$	5.92	0.29
Phlogopite, Edwards, N. Y....	$Al(SiO_4)_3Mg_3KH_2$	9.32	0.22
Laumontite....................	$Al_2SiO_4Si_3O_8Ca.4H_2O$	1.00	0.18
Lepidolite, Maine.............	$\left\{\begin{array}{l}KHLiAl_3(SiO_4)_3\\K_3Li_3(AlF_2)_3Al(Si_3O_8)_3\end{array}\right.$	13.00	0.18
Elæolite, Litchfield, Maine....	$Al_3(SiO_4)_3Na_3$	21.17	0.16
Heulandite, Nova Scotia.......	$Al_6(Si_3O_8)_6(CaNa_2)_3.16H_2O$	2.00	0.13
Orthoclase....................	$KAlSi_3O_8$	16.00	0.11
Analcite......................	$NaAl(SiO_3)_2.H_2O$	14.00	0.10
Oligoclase, Bakersville, N. C..	$\left\{\begin{array}{l}AlNaSi_3O_8\\Al_2CaSi_2O_8\end{array}\right\}$	9.18	0.09
Albite........................	$AlNaSi_3O_8$	12.10	0.07
Wernerite, St Lawrence Co., N.Y	$\left\{\begin{array}{l}Ca_4Al_6Si_6O_{25}\\Na_4Al_3Si_9O_{24}Cl\end{array}\right\}$	11.09	0.07
Leucite, Vesuvius, Italy........	$KAl(SiO_3)_2$	21.39	0.06
Stilbite, Nova Scotia..........	$Al_2(Si_3O_8)_2(CaNa_2).6H_2O$	1.00	0.05
Chabazite, " "	$Al_2SiO_4Si_3O_8(CaNa_2).6H_2O$	7.10	0.05

It is worth noting in comparing the depth of color produced by phenolphthalein solution, as shown in Professor Clarke's paper, with the percentage of alkali in solution as shown in this work, that some of the minerals which give a deep coloration with the former, show in the above table a comparatively small amount of alkali in solution, and *vice versa*. Muscovite for example while giving only a faint coloration with phenolphthalein, contained in solution alkaline compounds equivalent to 0.49 per cent. K_2O; pectolite, with 0.57 per cent. Na_2O, being the only one of the series showing a larger amount.

I hope in the near future to be able to carry this investigation further.

LABORATORY OF THE U. S. GEOL. SURVEY,
February 9, 1899.

[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY. No. 6.]

A METHOD OF ANALYSIS FOR CANNED CONDENSED MILK.[1]

BY F. S. HYDE.

Received February 17, 1899.

BEFORE proceeding with the analysis, it may be desirable to ascertain the approximate specific gravity of the sample as follows:

Weigh the can with its contents. Then remove contents, replace with water to the top, and weigh again. Weigh empty can (sufficiently dried) and ascertain weights of milk and water separately. Divide the weight of condensed milk by the weight of water as a standard, and the quotient is the specific gravity of the condensed milk (near enough for practical purposes).

The specific gravity, which is not a matter of great importance, may vary from 1.27 to 1.37, according to the quantity of cane-sugar added, or according to the relative amounts of fat and albuminoid material in the milk used for condensation. That is, milk deficient in fat may show an increment in gravity irrespective of the amount of sugar added.

As to the method of analysis: the contents of the can, together with any portions of crystallized sugar, which may adhere to the bottom of the can like a hard mealy mass, are transferred to a beaker and stirred vigorously until the mass

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[1] Read before the New York Section of the American Chemical Society, February 10, 1899.

becomes thinner and of the same consistency throughout. Then make stock solution as follows :

Stock Solution.—Weigh out twenty-five grams of the condensed milk and to this add seventy-five cc. water at ordinary temperature. This gives approximately 100 grams solution (of which twenty-five grams are condensed milk) of very nearly the consistency of cow's milk.

The writer attempted to simplify the method by taking aliquot parts of the stock solution for the various determinations, instead of weighing the different portions. Comparisons of the two methods gave discrepancies of three to five per cent. and the method of weighing was adopted as the more accurate, since an error of one-tenth cc. in measuring out five cc. for total solids may involve a difference of from one to two per cent. in the result. All results must be multiplied by four, since the condensed milk is diluted to one-fourth its strength ; *viz.*, each gram of solution should contain one-fourth gram of original condensed milk.

Total Solids.—Weigh out about five grams stock solution in previously weighed lead capsule (bottle cap two and one-half inches in diameter) or platinum dish. Evaporate on the water-bath to dryness. Finally heat in air-bath at 100° C. for fifteen minutes. Cool and weigh. Calculate the percentage and multiply by four.

Fat.—By Adams' coil, weigh quantity (five or six cc.) of stock solution in smallest beaker, recording weight of beaker and solution together. Without removing beaker from balance pan, insert the coil. When a sufficient quantity of solution has been absorbed, withdraw the coil, and reweigh the beaker with its residual contents. The difference is the weight of milk taken up by coil. Dry coil in air-bath at 100° from four to five hours, and extract with ether in the usual manner, employing a Soxhlet or Knöfler apparatus. Multiply the result by four.

Milk-sugar.—Dilute ten grams stock solution to 100 cc. Titrate direct with Fehling's copper solution. Calculate the percentage and multiply by four.

Cane-sugar.—Weigh ten grams stock solution in a No. 2 beaker. Add about fifty cc. water and five cc. (1 : 10) citric acid solution. Boil ten minutes. The citric acid inverts the cane-sugar, but not the milk sugar. Condensed milk solutions do not coagulate readily with citric acid, hence filtration is superfluous. Cool the solution and neutralize with a solution of caustic potash, using litmus paper, and make up to 250 cc. Titrate direct with Fehling's solution in casserole over low flame. Make a duplicate titration to check results. Calculate reduction as due to cane-sugar, and then deduct milk sugar in terms of cane. The Fehling's copper solution should contain 69.28 grams copper sulphate per liter (five cc. equal to 0.05 gram glucose). On mixing equal volumes of the copper and alkaline tartrate solutions:

Ten cc. should equal 0.0500 gram glucose.
Ten cc. should equal 0.0678 gram milk sugar.
Ten cc. should equal 0.0475 gram cane-sugar (by inversion).

Example:

Suppose 10.16 grams stock solution are taken, inverted, and made up to 250 cc. as above; and suppose, on titration, nine cc. of this diluted solution is found equivalent to 0.0475 gram cane-sugar. Then 250 cc. should contain 1.3194 grams cane-sugar, or 12.98 per cent. (if all sugar in 10.16 grams stock solution be calculated as cane). Since the stock solution is one-fourth the strength of the original condensed milk by dilution, then 12.98 per cent. cane-sugar multiplied by four equals 51.92 per cent. cane-sugar. Now deduct the per cent. of milk sugar in terms of cane-sugar. Assume that milk sugar has been found to be 12.796 per cent., which is equivalent to 8.96 per cent. cane-sugar; then 51.92 per cent. minus 8.96 per cent. equals 42.96 per cent. cane-sugar as such.

It will be observed that while the method of calculation is not new, yet the results obtained are dependent on the manner of making up the milk solution, and weighing the quantities taken for analysis, instead of taking aliquot portions, as in the old methods.

Casein, Albumen and Salts.—The difference between milk solids, and the sum of the milk sugar and fat, is casein, albumen, and salts. For proteids alone, make a nitrogen determination by the Kjeldahl method.

Water.—The difference between 100 per cent. and the per cent. of total solids gives per cent. of water.

Milk Solids.—Subtract cane-sugar from total solids.

Ash.—The content of ash varies with amounts of cane-sugar present. It may be determined by igniting total solids in a platinum dish.

Degree of Condensation.—This depends on the extent of condensation at factory, as well as the amount of total solids in the original cow's milk used. It is rather an uncertain figure, since skimmed milk might be used. Calculation is usually made by dividing the percentage of milk solids in the condensed milk by 12.5 per cent., the average for ordinary cow's milk. Some recommend calculation based on the percentage of 'solids not fat."[1]

In regard to the determination of cane and milk sugars in condensed milk with Fehling's solution, when the milk solutions are sufficiently dilute, the end-reaction may be easily determined without the use of the ferrocyanide indicator and the consequent loss of time in preparing ferrocyanide solutions and making filtrations will be avoided.

The condensed milk solution is titrated directly, without coagulation and filtration, in a four-inch casserole over a low Bunsen flame. When the titration is nearly completed it will be noticed that the red precipitate of cuprous oxide and organic matter seems to suddenly collect and settle, on removal of the heat, leaving a clear supernatant liquid which may be either bluish or yellowish, according as the titration is "under" or "overrun." This is all the more apparent in a casserole.

If the supernatant liquid is still slightly bluish, when tilted against the white sides of the casserole, a few drops more of the milk solution will discharge the color, such decolorization being the end-reaction. This end-reaction has been carefully compared with the ferrocyanide indicator, and the difference is too small to be of practical importance, when rapidity is an essential feature of the analysis.

With very little practice, the eye becomes accustomed to the change (discharge of color) and the value of the method can best be appreciated when it is necessary to execute several analyses in a short space of time.

Citric acid employed for the inversion of the cane-sugar, not-

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[1] See McGill: *Analyst*, May, 1898, p. 128.

withstanding statements of various authors to the contrary, usually does not produce coagulation in condensed milk solutions, even on boiling. Unless necessary to resort to prolonged operations for coagulation and filtration with special reagents, it is advisable to make use of dilute solutions directly, and avoid any errors in coagulation and filtration, which might not compensate for discrepancies in titration.

It is generally admitted that the presence of organic matter, other than sugar, exerts a reducing action on Fehling's solution while at the same time concentration by evaporation and rapidity of titration also influence the results, so that, whether coagulation and filtration are employed or not, the final results cannot be considered as absolute.

The amount of cane-sugar averages between thirty and forty per cent., and the fat below twelve per cent., which is not surprising in a manufactured article. In the so-called evaporated milks or creams, the cane-sugar is usually absent. The presence of cane-sugar seems to be essential as a preservative and to make the canned condensed milk palatable. Polarimetric methods may be employed for estimating the sugars, but extra reagents are required for clarifying the solutions, besides a correction for the volume of precipitated solids.[1] The old Fehling method is quicker and the results quite satisfactory. Again, it is claimed that the heating during the process of manufacture of condensed milk alters the rotatory power of the milk sugar, while its power to reduce alkaline copper solutions is not seriously affected.

In the Report of the Brooklyn Health Department for *1895*, p. 270, will be found a list of condensed milk analyses, which, with two or three exceptions, were performed by the writer according to the method submitted. The results are hereby appended for ready reference :

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[1] See Leffmann and Beam's Analysis of Milk and Milk Products, (*1896*), pp. 70–73.

CONDENSED MILKS ANALYZED DURING 1895.

Brand.	Total solids.	Milk solids.	Milk sugar.	Cane-sugar.	Fat.	Casein, albumen, salts, etc., by difference.	Water.
A......	77.56	40.78	14.04	36.78	9.53	17.21	22.44
B......	78.04	44.22	10.14	33.82	10.56	23.51	21.96
C......	75.12	41.96	15.71	33.16	8.92	17.33	24.88
D......	75.32	37.36	12.28	37.96	9.04	16.04	24.68
E......	76.72	36.72	9.50	38.00	8.84	20.38	23.28
F......	78.82	44.92	10.64	33.90	10.35	23.93	21.18
G......	74.72	41.71	13.12	33.01	7.84	20.75	25.28
H......	77.12	42.28	12.80	34.84	9.80	19.68	22.88
I......	77.72	45.81	11.96	31.91	9.52	24.33	22.88
J......	71.16	38.25	12.52	32.91	9.04	16.69	28.84
K......	76.40	39.91	11.92	36.49	8.68	19.31	23.60
L.....	79.12	47.29	11.06	31.83	10.38	25.85	20.88
M.....	75.64	42.73	17.20	32.91	9.18	16.37	24.36
N......	74.96	40.37	12.24	34.59	9.92	18.21	25.04
O......	77.56	43.21	10.76	34.35	8.40	24.05	22.44
P......	77.72	45.91	12.56	31.81	8.56	24.79	22.28
Q......	75.76	46.82	10.84	28.94	10.03	25.95	24.24
R......	73.72	30.76	12.79	42.96	8.07	9.89	26.28
S......	35.24	35.24	12.32	none	11.82	11.10	64.76
T......	34.33	34.33	11.27	none	9.76	13.30	65.67
U......	30.46	30.46	10.15	none	6.73	13.58	69.54

The last three analyses represent so-called "Evaporated Milks," containing no cane-sugar.

A law of New York State,[1] requires that no "condensed milk shall be made * * * * unless the proportion of milk solids shall be, in quantity, the equivalent of twelve per centum of milk solids in crude milk, and of which solids twenty-five per centum shall be fats."

Generally, the amount of fat in condensed milk is less than ten per cent. of the whole, or less than twenty-five per cent. of the forty per cent. (more or less) milk solids of which the fat is a part.

The original cow's milk used may be considerably above legal standard, and yet the degree of condensation be insufficient to bring the manufactured article within the requirements of the law. Under such conditions, the manufacturer might be liable to prosecution, although the product might be perfectly wholesome.

As to preservatives, the manufacturers seem to depend almost entirely on the use of cane-sugar in sufficient quantity.

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[1] Sec. 25, Chap. 143, L., 1894.

REVIEWS.

ON RECENT PROGRESS IN PHOTOCHEMISTRY.[1]

The term "photochemistry," as we intend to treat it, is to be taken in a broader sense than that which is usually accorded to it. It is proposed to express by it more than the influence which light exerts in stimulating chemical activity. The chemical manipulations, reactions, and general manifestations are all instrumental in bringing about the visible effects of this action and should not be isolated from it in treating the subject.

Let us confess at the outset that the influence which light exerts upon silver haloids is still enigmatical. We cannot even to-day say positively what occurs in this case, chemically speaking. It cannot be said without decisive proof that a subhaloid or a perhaloid has been produced, nor can we prove that silver has been reduced to the metallic state.

We may perhaps be permitted to suppose a transformation of the vibrations which we call light into those which may be called chemical vibrations.

When light vibrations impinge upon a mixture of hydrogen and chlorine, it is surely not merely havoc which results, but a rythmic system is produced. With bromine and hydrogen this action takes place in a similar manner, but at higher temperatures. Heat vibrations as well as light vibrations are here perhaps transformed into chemical vibrations.

It requires great strength of scientific faith to believe that in all these actions the light vibrations play merely the part of that famous tip of an eagle's wing, which, accidentally disturbing the repose of a snowflake, causes the avalanche to proceed upon its destructive path downward into the valley.

That light vibrations on impinging upon a chemical compound, such as silver bromide, turn latent within this compound without really decomposing it, has long since been virtually shown by the fact that those parts of a photographic dry plate, thus affected, really exhibit this condition by the readiness with which they are attacked by reducing agencies, suitably applied. This manner of looking at the developing of a photographic negative has never as yet been attempted, or if so, not to our knowledge.

This conception is in no way rendered invalid by the recent observation of T. Sterry, that an exposed but not developed dry plate may be freed from unchanged bromides by immersion into

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[1] Read before the New York Section of the American Chemical Society, December 9, 1898.

sodium hyposulphite solution, and after this has been done it may be developed in gaslight by a developer containing silver nitrate. Sterry assumes that in reality two latent pictures exist within the exposed film, the first of which he calls the inorganic, the second, just mentioned, the organic one. If our own conception is upheld this differentiation would be needless, because the hyposulphite solution does not dissolve the parts of bromide that had been altered, perhaps by reason of changed stress within the molecule.

The following facts pointing in the direction of the views above stated may be cited :

Attention in the first place is called to the well-known appearances concerning phosphorescence paint. It is impossible to believe that the light vibrations are merely "bottled up" within the luminous paint, for the light given off is never of the same quality as the light received.

A very simple experiment shows this: A glass plate, upon which a smaller ruby glass plate is allowed to rest, is coated with luminous paint and exposed to sunlight. After some time the plates are taken into a semi-dark room, and we observe, on removal of the ruby glass, that the part which has been covered appears bright lemon-yellow, while the rest of the plate shines with its peculiar lavender-colored hue.

The red waves have in this instance been changed into yellow ones. Or, if the ruby glass should have allowed yellow waves to pass through (which, however, is not likely) we must conclude that the red waves had been absorbed.

If we use for the purpose of expressing the difference of color between the light received and that emitted the terms, borrowed from electric terminology,[1] "step-up," and "step-down," we have in our experiment, just described, to do with a "step-up." With blue glass, under similar conditions, we obtain a more reddish yellow, a "step-down."

In order to show how the vibrations communicated in some way to the phosphorescent plates may be made to further exert their activity, I shall now refer to the experiments of Prof. Zenger, director of the observatory at Prague. Zenger exposed a phosphorescent plate in a camera, provided with a prism, to the solar spectrum. He obtained a picture of the same in its entire length, from ultra-red to ultra-violet. We may remark incidentally that Fraunhofer's lines appear on the phosphorescent plate as bright lines in the red and as dark lines in the violet part of the spectrum. Zenger proceeded then to face the phosphorescent plate in a printing frame, in the dark room, to a sensitive dry-plate. Later on he developed the dry plate and thus obtained a permanent picture of the spectrum.

[1] See W. Goold Levison: On a system of classification of luminescent substances, New York Academy of Sciences, December 5, 1898.

In speaking about phosphorescence we must not forget to call attention to the recent research of Wiedemann and his co-workers. The facts most interesting to us about these observations are those of transformation of radiant energy into chemical energy and vice versa of chemical into radiant energy. Wiedemann introduced a new terminology for the generic word phosphorescence. He calls all the pertaining phenomena collectively "luminescence," of which phosphorescence is only a special case.

We may call the fact of a body becoming luminous 'normal' if primarily the oscillations caused by the agency of heat are increased to such a degree, that different oscillations, which we recognize as light, are produced. But besides this kind of generation of light we know another one in which external causes, without corresponding increase of temperature, produce light. This second kind of exciting light Wiedemann calls luminescence.

Photoluminescence is then produced by light as an impinging cause. This, according to its persistence or to its instantaneous appearance, has to be termed phosphorescence or fluorescence. Electric discharges, causing light appearances in gaseous bodies, produce electroluminescence. We notice that Wiedemann found that even here the temperature lies frequently far below the temperature sufficient to cause the incandescence of such gases.

Light caused by certain chemical processes is called "chemiluminescence;" that produced by gentle warming, *e. g.*, of fluorspar "thermoluminescence." Light appearances caused by friction are called "triboluminescence;" by crystallization are called "crystalloluminescence;" and by solution, "lyoluminescence."

Without attempting to enter in detail upon this new and interesting field of study we allow our attention to be drawn to some experiments of chemical interest. Lenard and Wolf found that if a photographic negative, newly developed by means of (potash) alkaline pyrogallol and sodium sulphite, is slightly washed and then put into the alum-bath, in the dark, that in the first instance the plate and subsequently the entire bath appear highly luminous. They observed the phenomenon in developing a stellar photograph and sought for the cause. Chandler supposed the sensitive film to be the cause. Phosphorescence, induced by alumina precipitated by potash, was excluded. A true chemiluminescence was found to obtain. This luminescence, however, did not take place if alumina was not precipitated. We know that an excess of potash as well as of alum may prevent such precipitation. On the other hand, precipitation was not always accompanied by luminescence. If sodium sulphite or pyrogallol were left out of the solution, the most perfect precipitation without luminescence occurred.

In short, though the proportions of the developer were changed in many ways it was not only shown that sulphite must not be present in excess nor in too small quantities (above 1.25 per cent. or below 0.13 per cent.), in order to produce the effect; in the same way an excess of pyrogallol above 0.3 prevented it, but 0.005 per cent. pyrogallol sufficed to produce it. Evidently, in order to successfully perform the experiment, a fifth substance, not intentionally introduced into the developer, was at work right along. Observation showed that the precipitated aluminum hydroxide after luminescence had occurred, had carried down all the pyrogallol, the supernatant liquid was colorless, the precipitate yellow. Suspicion was aroused that alumina, in its finely divided condition, had fixed upon its surface not only all of the pyrogallol but also oxygen, which was proved to be the sought-for fifth substance. The luminescence was the consequence of a sudden energetic oxidation of pyrogallol.

The proof was rendered in many ways. The experiment was performed in presence and in absence of air. In the first case luminescence occurred, in the latter not. A further experiment was performed in presence of oxygen, when luminescence appeared brighter than ever.

A conundrum, however, was offered in the fact that sodium sulphite, an oxygen consumer, purposely added to developers to prevent spontaneous oxidation of pyrogallol (*e. g.*) was nevertheless necessary to bring about the phenomenon.

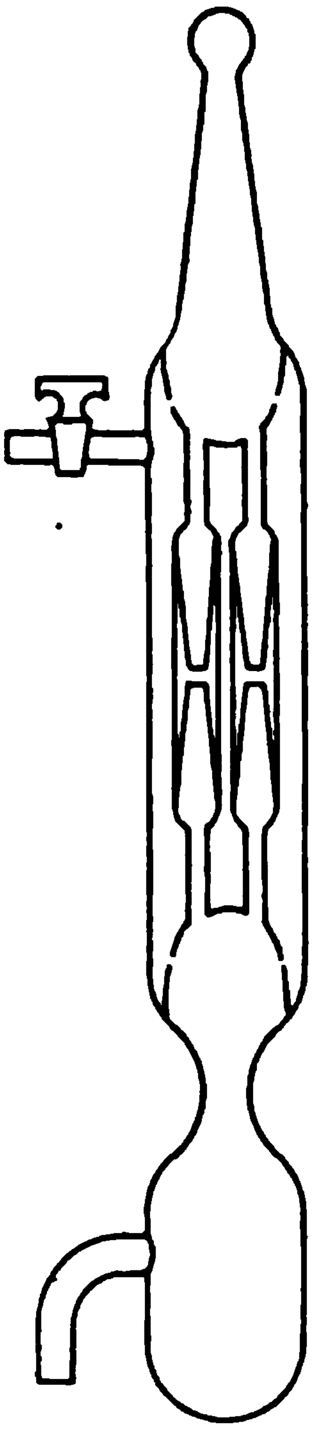
The curious fact was experimentally established that the pyro-sodium sulphite potash developer used up oxygen less swiftly than did pyropotash alone, thus the developer containing sulphite remains richer in free oxygen than without it.

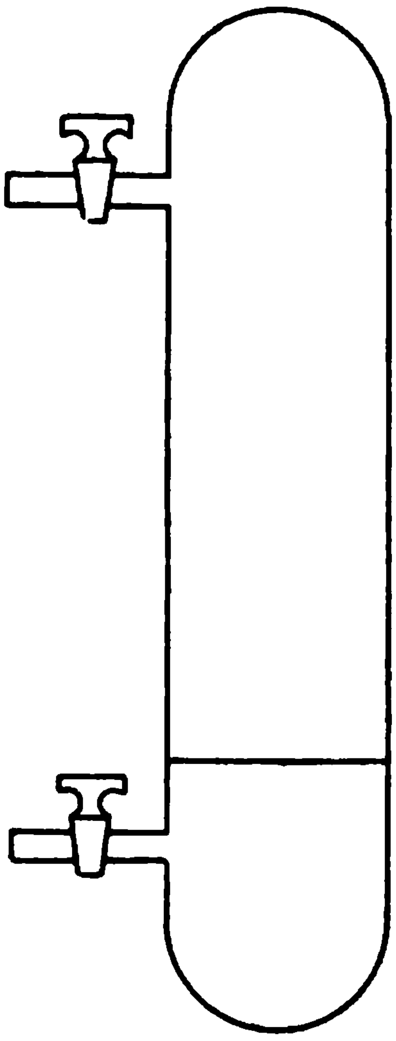
This is one example of true chemiluminescence caused by oxidation of pyrogallol.

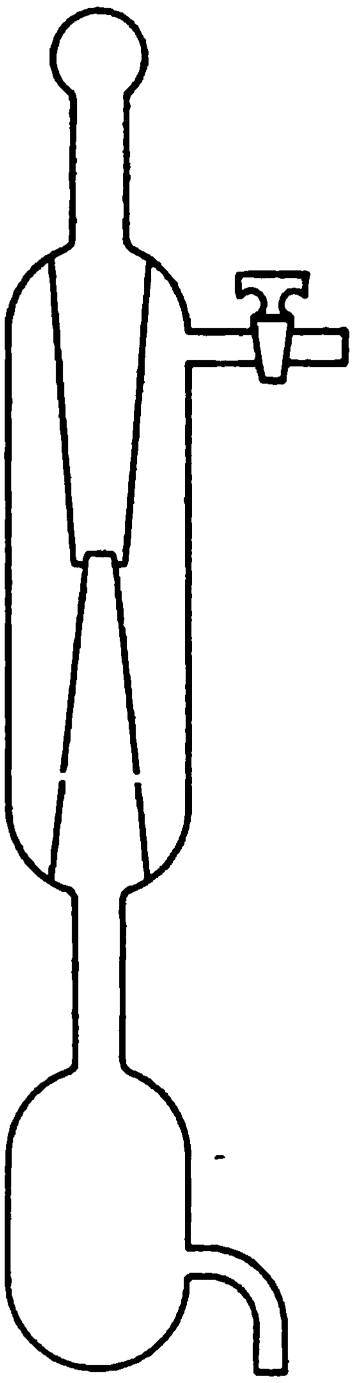
Another, still more interesting, example of chemiluminescence is offered by the appearance of what was formerly called "sea-phosphorescence." This luminous appearance of the ocean, according to newer researches of Otto, is the consequence of oxidation of organic matter by means of ozone. Water, introduced together with ozone into the apparatus shown in the accompanying figures, will turn highly luminous upon agitation. Distilled water will not show the effect, but upon addition of urine, alcohol, benzene, or other suitable oxidizable material, luminosity will appear.

It may be of use to those present interested in photography, to say a few words about the changes in developers. There is in the first place a developer to be mentioned, producing color tones in dia-positives for the purpose of projections. We all know how important a factor is the suitable color for a given picture.

Silver chloride gelatine plates should be used (similar to the mixture on the Aristo papers) and the plates are not printed out under the negative. The outlines of the picture must faintly show in daylight, to which they should be exposed for one to three minutes, according to the kind of light and of the negative. As a uniform developer, paramidophenol is recommended by Hanneke, of the Berlin-Charlottenburg photochemical laboratory.







Distilled water	1000 cc.
Crystallized sodium sulphite	50 grams
Citric acid	8 "
Paramidophenol hydrochloride	7 "

In this manner pictures in yellowish-brown tints are obtained; carmoisin, violet to steel blue tints, are produced subsequently in a gold-bath containing ammonium thiocyanate. Acetone and aldehyde are beginning to take the place of alkalies in our developers. The brothers Lumière and Seyewetz were the first to recommend these substances.

Water	500 cc.
Sodium sulphite (double usual amount to produce black tone)	200 grams
Concentrated sulphuric acid	10 drops
Pyrogallol	14 grams

Fifteen cc. of this and five cc. acetone and dilution to 50–120 cc. with water. Excess of acetone produces a greenish color. Acetone is said to harden the film. Consequently this developer is of importance for photographic work in tropical climates. It is not necessary to use C. P. acetone but the commercial product of boiling-point +56°–58° C., which costs about thirty cents per pound, suffices.

Bromide paper developed with acetone developer will be found free from blisters. The aldehyde developers, in contrast to the acetone developers, are rapid workers and they require an ample addition of potassium bromide.

Water	100 cc.
Sodium sulphite	15 grams
Formaline (forty per cent.)	2 cc.
Hydroquinone	1.5 grams

Ordinary ethyl aldehyde (fifty per cent.) can be used also, while benzaldehyde, acetophenone, and benzophenone, which can only be used in alcoholic solution, are practically useless. Dr. Andresen furnishes a list of reactions of the current developers. He includes in his list the following:

Amidol = Hydrochloride of 2,4-diamidophenol.
Eikonogen = α-Amido-β-naphthol-β-sulphonic acid.
Glycin = *p*-Oxyphenylglycin.
Hydroquinone.
Metol = Methyl-*p*-amidophenyl sulphate.
Ortol = Methyl-*o*-amidophenol sulphate, mixed with hydroquinone.
Paramidophenol hydrochloride.
Pyrogallol.

In regard to the use of formalin for photographic purposes it is a fact worth recording, that the expansion of paper, consequently any distortion whatever of the picture, may be avoided by previous immersion of the paper in a two per cent. formalin solution and subsequent drying.

The sensational news, which passed some time ago through our daily papers, embellished by appropriate pictures, suggestive of spiritistic productions, were based upon the observation of Dujardin, that imprints of the human hand may be produced within the developing bath upon dry plates. It was found that the animal heat produced these pictures and that a direct contact of the plate with the hand, only shielded by another glass plate, is necessary. If the covering glass plate was separated from the dry plate (both in the developer) by means of glass rods or glass cubes, no action occurred.

It is gratifying to the chemist to observe how chemistry enters in almost every direction as a handmaid into practical photochemical pursuits.

Lieutenant Kiesling has constructed a magnesium light apparatus, avoiding the smoke attending the use of this element. He allows salt-mouthed vials of 250-400 cc. capacity filled with dry oxygen (directly from the gasometer), and containing magnesium ribbon and a fuse, or an electric wire system, to oscillate like a pendulum. The bottom of the little vials is covered with a small quantity of plaster of Paris or asbestos. It is said of magnesium burnt in oxygen that it furnishes a light the actinic action of which is twelve times as great as if burned in air. The little vials remain useful for twenty-four hours. Acetylene light has also been recommended.

Dr. Roberts, Director of the Archæological Museum in Halle, observed that in a collection of silver coins of the fifth century B.C. (Tetradrachms) had suffered a change on the surface of the side exposed to light. The analysis of the thus changed surface proved this to consist of silver chloride. An attempt is made to explain this by showing that these coins had for centuries been resting in sand containing NaCl. A coinage from silver containing silver chloride is excluded since the interior parts of the coins were proven to consist of tolerably pure silver.

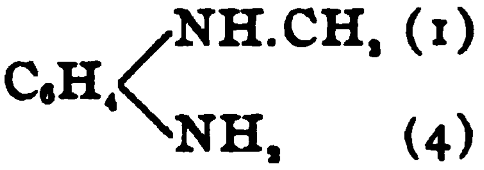
A comparatively new field of research is opened up by the study of what makes an organic substance a developer. What are the groups with developing functions? A. and L. Lumière and Seyewetz have studied the influence in this direction of alkyl-substitutions in groups possessing developing functions.

As a general rule it has been granted that the faculty of developing the so-called latent picture, exists in compounds containing at least two hydroxyl groups in ortho or para position.

These authors have studied the para-compounds of amidophenols and of polyamines for which the above rule was still under discussion.

Paraphenylendiamine and paramidophenol were subjected to alkylization, and the following substitution-products were prepared and tested in regard to their developing properties:

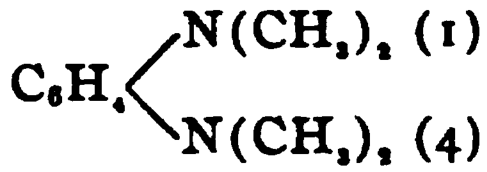
1. Monomethylparaphenylenediamine,



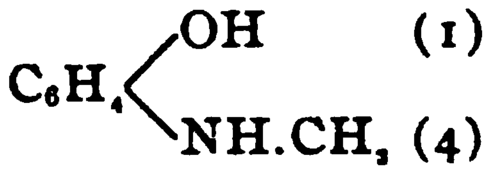
$$C_6H_4\left\langle\begin{array}{ll}NH.CH_3 & (1)\\ NH_2 & (4)\end{array}\right.$$

2. Dimethylparaphenylenediamine, 

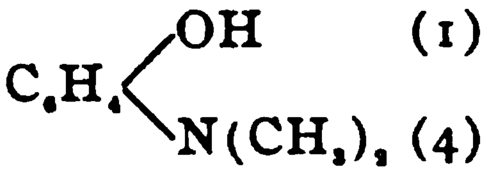
$C_6H_4\left\langle\begin{array}{ll} N(CH_3)_2 & (1) \\ NH_2 & (4) \end{array}\right.$

3. Tetramethylparaphenylenediamine, 

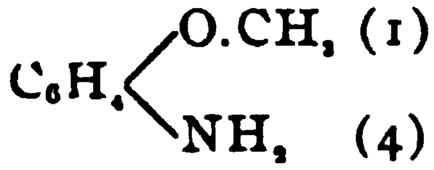
$C_6H_4\left\langle\begin{array}{ll} N(CH_3)_2 & (1) \\ N(CH_3)_2 & (4) \end{array}\right.$

4. Monomethylparamidophenol, 

$C_6H_4\left\langle\begin{array}{ll} OH & (1) \\ NH.CH_3 & (4) \end{array}\right.$

5. Dimethylparamidophenol, 

$C_6H_4\left\langle\begin{array}{ll} OH & (1) \\ N(CH_3)_2 & (4) \end{array}\right.$

6. Paranisidine, 

$C_6H_4\left\langle\begin{array}{ll} O.CH_3 & (1) \\ NH_2 & (4) \end{array}\right.$

The compounds 1 to 5 are developers. 1 to 3 may even be used as such without the addition of alkali. 6 was without developing power.

The alkylization, as far as shown, therefore, does not destroy the developing power. We must remember that the alkyl-substitutions into an amido group weaken its basic properties but do not entirely destroy them. On the other hand, if a hydroxyl of a phenol suffers alkylization the phenol properties are lost entirely (as in 6), as are the acid properties in most neutral salts, and the developing power is correspondingly lost.

Leaving the chapter of the chemistry of developers we record a number of various items of general interest.

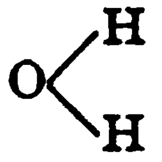
Glycerol has been successfully used instead of alum in electric light projection. The lenses as well as the diapositives are endangered by the high temperature of the arc light. For the celluloid films of the kinematograph this danger is obvious. The alum cell heretofore used is sometimes brought up to boiling and in the best case it will form bubbles. Glycerol has been used even between the source of light and the condensing lens. After a performance of two hours under these conditions with an electric lamp of 2000 candle-power, the glycerol (which does not form bubbles and boils at +290° C.) registered +80° C. Pure glycerol being practically colorless, the light is not in any way weakened.

Talking about the kinematograph, it may be worth while reminding this audience of the immense proportions which the applications of photochemistry have assumed in this country. Mr. Dunn ordered from the Eastman Co. three kinematograph films, each 50,000 feet long. Each film was said to cost $10,000. The films were intended to be used at the occasion of the Corbett-McCoy contest in Buffalo, and three apparatus to work simultaneously in order to secure at least one good copy. Each film of 50,000 feet was supposed to run for eighty minutes (625 feet per minute) and twenty-seven pictures were to be taken per second.

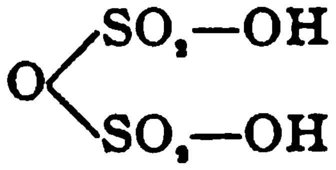
The use of the most varying chemicals for photochemical pursuits is surely on the increase and it happens frequently, as we stated at the outset, that the chemist is confronted with reactions quite difficult to understand.

A case of this kind is offered in the use of ammonium persulphate for the purpose of softening hard negatives. This technical term means, in common language, that a negative which shows too strong contrast between high lights and shadows has to be brought down to more uniform delineation by chemical action. Mechanical rubbing down of the denser parts by means of alcohol, or local or entire reduction (as it is styled) by means of potassium ferricyanide and sodium thiosulphate, were tedious and sometimes doubtful modes of procedure.

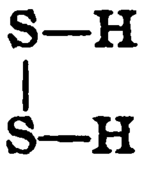
The ammonium persulphate in a five per cent. aqueous solution has the faculty of attacking the denser parts, without injuring the detail in the shadows of the negative. Ammonium persulphate is a salt of persulphuric acid. We are in this instance agreeably reminded of Kekulé's lucid way of showing at a glance the similarities in the constitution of compounds.



Water.

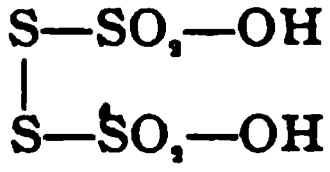


Disulphuric acid (or pyrosulphuric acid).



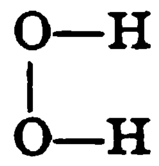
$$\begin{array}{l}\mathrm{S{-}H}\\ |\\ \mathrm{S{-}H}\end{array}$$

Hydrogen persulphide.



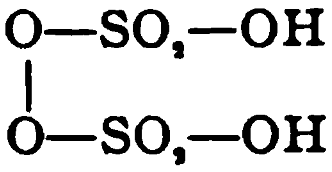
$$\begin{array}{l}\mathrm{S{-}SO_2{-}OH}\\ |\\ \mathrm{S{-}SO_2{-}OH}\end{array}$$

Tetrathionic acid.



$$\begin{array}{l}\mathrm{O{-}H}\\ |\\ \mathrm{O{-}H}\end{array}$$

Hydrogen peroxide.



$$\begin{array}{l}\mathrm{O{-}SO_2{-}OH}\\ |\\ \mathrm{O{-}SO_2{-}OH}\end{array}$$

Persulphuric acid.

The acid itself has not been prepared, but its salts are in use as oxidizers. They are mostly prepared from ammonium persulphate, which is obtained by electrolysis of ammonium sulphate.

The action of ammonium persulphate upon a negative is still under discussion. While some claim that a soluble double salt, $NH_4O.SO_2.OAg$, is formed, others assert that ozone is generated, as with hydrogen peroxide.

There is a chance for still further study. We cannot conclude this brief summary without referring to the action of most varying substances upon dry plates. Not only do certain vapors, but also matter from which no material vaporization can otherwise be noticed, attack the sensitive film of a photographic plate.

Messrs. Muraoka and Kasuya, in Kyoto, Japan, made a study of the light of glow worms. In addition, they experimented in the direction just now referred to. I quote their own words: "We also experimented with magnesium oxide and cadmium oxide. The first has no action, but the latter shows a curious behavior, inexplainable either by radiation or vaporization. We took two thick pieces of card-board, A and B, both of the size of a photographic dry-plate; from the center of A we cut out a small square and from that of B a large square. A was put upon a glass plate and the square cut away was filled with powdered cadmium oxide. Then A was covered with B and the dry-plate was put on top of B. We expected to find that the plate would be attacked all over the area of the larger square of B, since the vapor from the smaller opening could have easily spread to the edges of the larger square. But on developing the plate it was found that the blackening was restricted to the size of the smaller square.

If A is separated from B to the distance of 1 cm. and a copper wire is stretched between the two without touching them, no blackening will be produced above the copper wire. According to this, a radiation appears to be at work, but it remains inexplainable why this radiation does not also obliquely extend to the larger square."

It may interest you to hear of experiments performed by myself with the view of practical application. I faced daguerreotypes to dry-plates in a printing frame and obtained faint but very clearly outlined copies. These copies became more distinct, very likely by contrast, when I exposed the frame to light, the dry-plate being thus blackened to the extent of about two inches all around the impression made by the daguerreotype.

References: Photographische Mitteilungen, January, 1898, to November, 1898.

Annalen der Physik und Chemie, 64, No. 1 (*1898*); 34, No. 7, (*1888*); 34, No. 8*b* (*1888*).

College of the City of New York,
December, 1898.

L. H. Friedburg.

A REVIEW OF THE PRESENT KNOWLEDGE OF SODIUM NITRATE, TOGETHER WITH THE ORIGIN, PRODUCTION, AND DESTRUCTION OF NITRATES IN THE SOIL.

The importance of nitrates in technical processes, as well as in providing a quickly and certainly available plant food for admixture with chemical fertilizers, or for use alone, by the agriculturist, cannot well be overestimated. It is comparatively a few years since the vast stores of sodium nitrate in Chili have been sufficiently exploited to impress the world with their importance as a source of supply for the above demands, and I apprehend that the president of this society felt that it would not be time wasted when he invited me to direct the attention of the society to the origin, and to some of the uses of sodium nitrate, and also to some of the recent extensions of scientific knowledge in regard to the production of nitrate within the soil.

The rate at which the use of sodium nitrate is increasing in the United States, is shown by the following:

In 1897 the deliveries for January alone were 60,000 bags.
In 1898 " " " " " " 80,000 "
In 1899 " " " " " " 90,000 "

The yearly consumption in the United States for 1897, was 700,000 bags; for 1898, 975,000 bags. The total consumption of the world for 1897, was 8,050,000 bags; for 1898, 9,235,000 bags. A bag is approximately 300 pounds. The increased consumption in this country during the past year was 275,000 bags. These figures refer only to the Atlantic ports.

It speaks volumes for the influence of scientific men upon the development of practical agriculture in the world, when we remember that it is scarcely ten years since the agricultural experiment stations and scientific investigators began to vigorously direct public attention to this source of plant food. In fact, in this country, it has scarcely been so long, and it is only within the last two or three years that our experiment stations have been able to readily procure it.

There are two reasons for this rapid development:

(1) The almost absolute certainty of securing satisfactory results when a scientific man or a farmer uses it for experimental or practical purposes.

(2) The wonderful influence it has had upon the development of the beet-sugar industry in Germany and other parts of the world.

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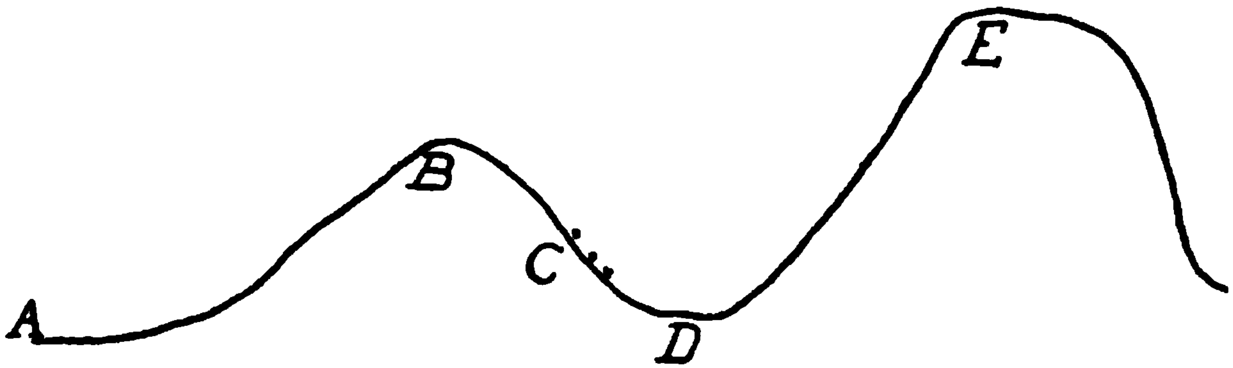
[1] Read before the New York Section of the American Chemical Society, February 10, 1899.

Its action upon vegetation is so certain and so uniform, and the demand of crops for additional supplies of it in the soil is so universal, that an experiment station can scarcely mistake in recommending the use of sodium nitrate, where the conditions affecting the production of bountiful crops are obscure. It is probably the most stimulating fertilizer in the market, and while the most satisfactory results can be obtained from it when in combination with ample supplies of available phosphoric acid and potash, which if not already found in the soil, should be applied to it in order to secure most bountiful harvests, yet as a special fertilizer a moderate application of nitrate alone, on most soils, proves highly remunerative.

At present, the entire supply of sodium nitrate comes from Chili, although it is found in some other parts of the world, but not in sufficient quantities to compete in the markets of the world. The portion of the west coast of Chili, where it is found, between latitudes 19°12′ south, and 25°45′ south, extends over a length of approximately 260 geographical miles. The principal deposits are found in the provinces of Tarapaca and Antofagasta, in Chili, and the center of trade is Iquique. It exists in a long, narrow strip, averaging about two and one-half miles in width, extending along the eastern slope of the Coast Range, at an average distance of perhaps fourteen miles from the ocean, but in a number of cases it is probably as much as forty miles from the coast. The region where it is found is a rainless desert, absolutely devoid of vegetation. The nitrate beds exist at a height of from 3,000 to 5,000 feet above sea-level, and extend down towards the valley of Tamagruel. The following rough sketch, not drawn to scale, will serve to illustrate the characteristic surface of the portion of Chili where the *caliche* is found. It will be seen that it lies between the Coast Range and the Cordillera.



A = Pacific Ocean ; B = Coast Range of Mountains ; C = Location of *Caliche* Beds ; D = Valley of Tamagruel ; E = Cordillera.

I cannot undertake the discussion of all of the theories in regard to the origin of these beds, but suffice it to say that the most satisfactory explanation seems to be that they have resulted from the decay of enormous quantities of organic matter particularly seaweed which probably accumulated in a long, narrow strip of water, somewhat like Core Sound on the coast of North Carolina.

This accumulation, in the course of ages, was elevated. One of the evidences of this lies in the fact that the remains of seaweed are found in the nitrate deposits. The beds are 500 or 600 feet above the valley of Tamagruel, and extend down toward it, decreasing in value as they approach it, until they finally disappear upon reaching it. The beds exist under the following conditions, and skilled prospectors can generally locate the beds with considerable certainty by the surface indications:

The surface for a depth of approximately ten inches is covered with a layer of fine, loose sand; under the sand is found a layer of amorphous porphyry, feldspar, sodium chloride, and other mineral matter, cemented together by gypsum into a compact mass varying in thickness from six to ten feet. This is called *costra* or crust. Under this crust is found the *caliche*, or impure sodium nitrate, varying in thickness from a foot and a half up to about twelve feet. The *caliche* occurs in a great variety of colors, as yellowish white, orange, blue-gray, and dirt color. This deposit is a regular stratum, with all the appearances of a rock formation, firmly cemented together, and is displaced from its natural position, by blasting. The system of blasting is peculiar in this, that they drill a hole through the crust and through the *caliche*, down to the clay surface beneath, large enough to admit a boy, who is let down and excavates the clay under the *caliche*, so that the blast can be placed under the material to be broken up, the object being to thrust up as large a mass of *caliche* as possible. This is then broken up by the tools of the workmen into chunks the size of an orange, and the impurities as carefully removed by the process of selection, as possible. This crude material is then transported to the works where it is run through a crusher, and dissolved in hot water. The better quality of *caliche* contains from forty to fifty per cent. of sodium nitrate. The average quality from thirty to forty per cent. of sodium nitrate, and the poorest quality that is worked, from seventeen to thirty per cent. of sodium nitrate. The best quality of *caliche* runs about as follows:

	Per cent.
Sodium nitrate	50
Sodium chloride	26
Sodium sulphate	6
Magnesium sulphate	3
Insoluble	14
Sodium iodate Sodium nitrite Magnesium chloride Potassium chloride Magnesium nitrate	1
	100

Under the present depressed condition of the industry, it is not profitable to mine *caliche* with less than about thirty per cent. of nitrate. The refining of *caliche* and the extraction of the sodium nitrate, depends upon the fact that sodium nitrate is very much more soluble in hot water than in cold water, while the solubility of salt in water, is little increased with increased temperature. However, the solubility of the nitrate in water at 20° C. is affected by a solution of salt, and while 100 parts of water, at 20° C., should dissolve 88 parts of sodium nitrate, when it contains 25 parts of sodium chloride in solution, it will dissolve only 52.8 parts of sodium nitrate.

The time at my command does not permit me to go into the details of the three systems in use in carrying out the solution, crystallization, and drying of the sodium nitrate. The crystallized sodium nitrate is removed from the mother-liquor and allowed to drain some time, after which it is put into sacks, where it drains still further, for a certain length of time, and the granulated appearance of the sacks as they come into our market is due to the crystallization of this drainage material upon the outside of the sacks.

The mother-liquor, from which the first crop of crystals is taken, can be used for dissolving a fresh supply of *caliche*, but it is not practicable to use it more than twice or three times. This mother-liquor which contains the impurities of sodium nitrate is worked over for the iodine contained in it. In fact, all of the iodine in the market at present, is produced as a by-product in the refining process of sodium nitrate, and could be thrown upon the market in such large quantities, that the price of iodine would be reduced to a very much lower figure, were it not for the fact that it is under the control of a combination, which regulates the output.

There is another product that might be secured, if some one could devise a profitable and sure method of manipulating it, and that is the sodium perchlorate. In some of the mines an appreciable percentage of sodium perchlorate is found mixed with the nitrate, and the chemist who can devise some cheap and effective means of extracting the perchlorate, will undoubtedly find it a very profitable discovery, as its presence is highly objectionable when found in the sodium nitrate, whether it be used as a fertilizer or for technical purposes.

There are two grades of sodium nitrate in the market: One grade, containing not less than ninety-six per cent. of sodium nitrate, or over sixteen per cent. of nitrogen, is imported for technical purposes,—manufacture of chemicals, and chemical industries. Then there is the second grade, called ninety-five per cent. nitrate, which contains not less than fifteen per cent. of nitrogen, imported more especially for fertilizer purposes. The sodium nitrate as it comes into this country is of very uniform composition and can generally be relied upon to analyze very close to the figures given. It generally contains from one per cent. to two per cent. sodium chloride, which is largely due to the difficulty of crystallizing out the sodium nitrate on a large scale without also securing a little of its impurities. Where it is desired to have purer nitrate than is produced at the works, it should be recrystallized.

Sodium nitrate is used

(1) As a special fertilizer.
(2) In compounding complete fertilizers.
(3) In the manufacture of sulphuric acid.
(4) In the manufacture of nitric acid.
(5) In the manufacture of nitrate of potash.
(6) In the manufacture of arseniate of soda.
(7) In the manufacture of fireworks.
(8) In the manufacture of fusing mixtures.
(9) In the purification of caustic soda.
(10) In the manufacture of steel.
(11) In the manufacture of glass.
(12) In the manufacture of minium.
(13) In the curing of meat.
(14) For making chlorine in the manufacture of bleaching-powders.

From the above list of the uses to which sodium nitrate is put, it will be seen at once that it plays a very important part in the industrial development of the country, and the question naturally comes up, "How long will the available supply last?" As I showed above, the consumption amounts to approximately 1,000,000 tons a year. There are at present exploited in Chili, beds of *caliche* estimated by different geologists to contain from 63,000,000 to 120,000,000 of tons of nitrate, and it seems that only a very small proportion of the territory where nitrate is likely to be found has yet been exploited, so that we need have no fear of the supply giving out during the next generation.

I have devoted considerable time to a review of facts, some of which are doubtless familiar to all of you, but all of which are probably not familiar to all chemists and are not readily accessible to many. Its use as a fertilizer, as it becomes known, will undoubtedly extend very widely. At present prices, it is perhaps the cheapest source of nitrogen in our markets.

But I must now turn my attention to another phase of the question, which is forced upon us by the rôle that sodium nitrate plays in agriculture. Agricultural chemists in particular have been laboring for years upon the problem of furnishing some cheap, natural means of producing nitrate rapidly, and in season for agricultural uses. It has been demonstrated beyond the shadow of a doubt that the majority of agricultural crops appropriate their nitrogen in the form of nitrates, a few being able to utilize it to a limited extent in the form of ammonia or humate of ammonia, and still others being able to secure their nitrogen supply by the action of micro-organisms which develop tubercles upon their roots, and enable them in this way to appropriate supplies of nitrogen which may be secured from the air or from nitrogenous compounds decomposing in the soil. There has sprung up, in connection with the study of these problems, almost a new branch of chemistry; that is, the study of the chemical reactions evolved by microscopic life.

Stutzer and Hartleb have shown that all cultivated plants, with the probable exception of the leguminosæ, appropriate their food in the form of nitrates, which are derived either from the fertilizers applied to the land, or from the nitrogenous substances in the soil which are converted into nitrates by the action of nitrifying bacteria. It has not yet been shown exactly in what form the nitrogen, appropriated by the leguminosæ through the bacteria existing in the tubercles upon their roots, is finally appropriated by the plant. It is, however, certain that the tubercles upon plants of this class are not able to appropriate the nitrogen from nitrates more freely, if indeed as freely, as they can from the free nitrogen of the air or soil. These tubercles upon the roots are the laboratories of the plant, apparently for the purpose of transforming the nitrogen of the air into suitable plant food for that class of plants. It is also quite well established by numerous investigators that the micro-organisms found in these tubercles have the power of producing within the soil where the plants grow, a capacity for storing up nitrogen, either in the roots of the plants themselves, or in the soil immediately surrounding them, in a form which can be appropriated as plant food by succeeding crops. Thus, crops of clover or peas, beans, vetches, serradella, lupines, and similar plants, apparently cause an accumulation of available nitrogen in the soil where they grow. The amount of this nitrogen accumulated from year to year is not large, but is sufficient to produce a perceptible effect upon the succeeding crop, and if it were possible by this means to continue indefinitely the growth of crops of this character upon the same land, it might be possible to fertilize the land by means of clover, peas, or other green manures of this character up to the point where maximum crops could be secured without the addition of fertilizers from other sources. These crops (especially clover) are looked upon with much favor in sections of our country where extensive farming, in contradistinction to intensive farming, is largely pursued. Not only do these crops, whether in the form of green manures plowed under, or simply as nitrogen storers, accumulate nitrogen within limited margins, but they also improve the physical condition of the soil, so as to enable the succeeding crops to more readily secure plant food existing in the soils. The importance of these nitrogen storers to the development of agriculture cannot therefore be overlooked, but as it is not evident that they derive their nitrogen from, or convert it into, any form of nitrate before the plant appropriates it, I will not enter further into the discussion of their use.

Hellriegel and Wilfarth found that certain soils would not produce satisfactory crops of these nitrogen gatherers unless they had been derived from fields where these crops had been grown, even when provided with abundant supplies of nitrogen in the form of organic compounds, or of nitrate. These pots, however, could be made to produce luxuriant growths of these nitrogen gatherers, if watered with the extract of the soil where the plants had grown. If the plants were watered with the sterilized solution of the soil, no growth was produced. The same pots, however, would produce a growth when watered with the unsterilized solution of the soil.

Nobbe went one step further, and reasoned that these unfruitful soils could be made fruitful if inoculated with the micro-organisms existing in, and probably producing, the tubercles. His experimental work was carried out with a view of determining the truth or falsity of this hypothesis. Operating upon sterilized soils containing ample supplies of available plant food, he found that his nitrogen gatherers would not grow beyond the point where they derived their supplies of nitrogen from the seed in sterilized soil, and that no tubercles were developed upon the roots of these plants. If, however, the soil was treated with a solution of pure culture of the bacteria existing in the tubercles, it immediately became fruitful and developed plants with abundant root tubercles. He found further that while the pure cultures indicated that the micro-organisms existing in the tubercles of the various nitrogen growers appeared to be the same under the microscope, yet they were not capable, except in a minor degree, of producing tubercles upon other members of the leguminosæ. For example :

The pure culture derived from the tubercles of the pea would produce tubercles upon the different varieties of peas, but might have little or no effect upon beans, or upon clover. So that he arrived at the conclusion that each plant had its particular class of micro-organisms capable of producing ample supplies of tubercles upon the roots of its own or closely related species, but incapable of producing tubercles upon plants remotely related to it. In connection with carrying out this idea in its practical applications, he set to work to prepare pure cultures of the organisms characteristic of the above plants, and a company has been organized in Germany for the preparation of these pure cultures upon a commercial scale. The medium employed is agar-gelatine. This is inoculated with the germs derived from the tubercles of the clover, the lupine, the pea, etc., as may be required, and is furnished under the name of *Nitragin* for the inoculation of soils with proper germs for the production of the desired crop.

The inoculation of the soil with these germs is effected in two ways:

(1) By moistening the seed with a solution of the inoculated agar-gelatine.

(2) By moistening dust or fine earth with a solution of inoculated agar-gelatine, and working it into the soil.

Probably the best results have been obtained from the latter process.

It has been found, experimentally, that soils which would not produce particular crops of these nitrogen gatherers before inoculation, could, in some cases, be made to produce fair crops by the inoculation. As a scientific curiosity it is of great value. In practice, however, it has failed to yield satisfactory results, and the time does not yet seem to have arrived when this system can be economically applied by the farmer. It should be remembered, also, that this principle applies only to the nitrogen gatherers, or plants deriving their nitrogen supply through tubercles. It costs about two dollars an acre to properly inoculate a field with the organisms necessary to produce any particular kind of leguminous plant. The uncertainty of the inoculation proving successful is so great, that Prof. Paul Wagner, Director of the Darmstadt Experiment Station, Germany, recommends the farmers of that country not to attempt it.[1]

Caron-Ellenbach has gone one step farther than the above, and has attempted to increase the capacity of the soil for directly absorbing nitrogen from the air. He has isolated and produced the pure culture of an organism which he has christened *Bacillus-Ellenbachensis α* which he finds possesses, in high degree, the power of causing the soil to absorb atmospheric nitrogen and transform it into available plant food. His claim is that soil inoculated with this bacterium increases its capacity for yielding up nitrogen in an available form for cereals and other crops, and that it absorbs large quantities of nitrogen from the air, and produces ample supplies for the use of the plants without resorting to expensive commercial fertilizers. .The pure culture of this bacterium is also manufactured on a commercial scale by a firm at Elberfeld, Germany, and is sold under the name of *Alinit*. This preparation, like *Nitragin*, has in practice been found to be a scientific curiosity, but while *Nitragin* has considerable experimental evidence to show that it frequently may

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[1] The most successful work done in this country upon this subject is by J. F. Duggar, Ala. Exper. Station Bull. No. 87.

increase the production of the leguminosæ, there is not, so far as I have been able to discover, any appreciable amount of scientific evidence to substantiate the claims set up for *Alinit*. In fact the *Bacillus-Ellenbachensis* α seems to be such a delicate creature, that the probability of its ever attaining any prominence in increasing the world's production of cereals, is relegated to the distant future.

While both of these discoveries are of great scientific interest, neither of them, I think, can be considered as anything more than demonstrating the fact that scientific men are working along very close to the lines where scientific discoveries of great practical value might be made.

Could the result sought to be attained above, be successfully and economically accomplished, the perplexing nitrogen problem would be solved for the farmers, but as they have not accomplished the results, it is necessary for scientific men to look further. The most promising field at present seems to me to be the study of the soil conditions which promote the rapid formation of nitrates, because that is the objective point to which we must direct all of our energies before we can expect to have any fertilizer, or any source of nitrogen supply utilized by the plant. We may have present in the soil, an abundant supply of nitrogen, and yet the plant may starve to death for nitrogen, because it exists in an unavailable form and cannot be converted into available form in time for the plant to utilize it.

The meteorological conditions most favorable to the production of nitrates are quite well known. But these we cannot control. It is demonstrated that there is a continual change going on in the supplies of nitrates present in the soil. They are carried down by the heavy rains, and they rise to the surface as the soil dries, so that there is a continuous movement of them in the soil. If the supply is ample, it is shown by a dark-green, luxuriant growth of vegetation. If it is inadequate, it is indicated by a stunted growth, and a yellowish-green color. The experimenter, therefore, is always in a position to determine, approximately, whether his plants are securing a sufficient supply of nitrates.

Until comparatively recently, the methods of analysis for detecting nitrates were not sufficiently delicate to throw full light upon the problem. Since, however, it has been discovered that the sulphate of diphenylamine is a sufficiently delicate test for nitrate to indicate one part in 100,000,000, it has been possible to shed much light upon the movements of nitrates, and the existence of nitrates in agricultural plants. Serno has found nitrates in almost all families of plants. The largest quantities occur in Malvaceae, Cruciferae, Papervaceae, Convolvulaceae, Labiatae, Compositae, and Urticaceae. In many plants it occurs only in the roots, and more especially only in the newly formed, absorbing roots. He finds that it is stored in the roots during the winter in some; in others it is found only in the spring. In annuals the nitrates occur abundantly in all parts.

Deherain has found that wheat will store as much as one per cent. of nitrates in the roots of the plant during the winter time, and that if the dry roots be dipped in a solution of the sulphate of diphenylamine, they take on a deep blue color, indicating the presence of a very large percentage of nitrates retained in the roots preparatory for use when growth starts in the spring. Damussy has found that these nitrates are not washed out from the roots by cold water, although they are readily extracted by warm water, or when the roots are subjected for some time to an atmosphere of chloroform and then washed with cold water. This, he thinks, indicates that the nitrates are held in the roots in some very unstable compound, perhaps with the protoplasm, and resume their normal condition whenever the protoplasm is modified by an elevated temperature, or by chloroform.

Serno is of the opinion that nitrates stored in the roots of plants during the winter, which, as growth begins in the spring, may be traced into the stems of the plants as they move up to the leaves and finally lose their identity in the leaves, are converted by the changes taking place in the growing plant, into some form of amides, especially, perhaps, asparagine. Our methods of analysis, however, are not sufficiently perfected to trace these compounds exactly to the point where this change takes place. They can be followed up the plant in the spring, quite distinctly in the roots, less distinctly in the stem, and they gradually disappear as they rise. This principle applies to a very large number of agricultural plants, and the power of these plants to store up nitrates in their roots is of great advantage in keeping a supply of available nitrogenous plant food within reach, which would otherwise have been washed out of the soil by the fall and winter rains. It is familiar to all of us that the nitrates form in greatest quantities during the moist, warm summer months, and that they exist in the soil in largest proportions in the latter part of the summer. This storing capacity of plants therefore is of great importance.

S. Winogradsky has devoted a large amount of time and attention to the study of the nitrifying organisms which convert ammonia salts into nitrates. He began by operating upon the soils around Zurich, and has extended his investigation to cover samples of soil taken from many countries of the world and from all climates. He has succeeded in isolating and preparing the pure culture of a group of organisms, called by him 'nitromonas,' which he is disposed to consider rather as a group of bacteria than as a single species whose special function is the oxidation of ammonia. He had already isolated bacteria whose special function was the oxidation of sulphur compounds and also the oxidation of iron compounds, which he named respectively 'sulfo-bacteria' and 'ferro-bacteria.' He therefore named these producing nitrate, 'nitro-bacteria.' He found that the nitromonas secured from different parts of the world possessed varying degrees of intensity of action. In the pure cultures, those from Europe acted slowly, and after a few generations of pure cultures, lost the power of oxidizing ammonia salts, while those secured from the soils of South America and Africa attacked the ammonia salts with great energy and seemed to acquire greater activity with successive generations. He has done an immense amount of work in the study of these bacteria, and has shed much light upon the peculiarities of their actions.

He also found that the nitromonas developed normally either in the light or darkness, and that they can assimilate the carbon from carbon dioxide in entire darkness. They are able, in entire darkness, to appropriate this carbon from carbonates or from carbon dioxide, and cause it to combine with the nitrogen to form organic matter, without the aid of the sun's rays. He believes that some sort of an amido compound is produced at the expense of the carbon dioxide and the ammonia. These chemical changes developed by the nitromonas, differ materially from those which occur with chlorophyl. In the action of chlorophyl, carbon dioxide is decomposed by the sun's rays, the oxygen liberated, and the carbon unites with the hydrogen and oxygen to form carbohydrates, but the investigations of Winogradsky indicate that the nitro-bacteria, instead of decomposing the carbon dioxide and setting oxygen free, effects its union with ammonia and makes use of the oxygen of the air to oxidize the nitrogen to nitrous and nitric acids, the energy for this change being supplied to them from the oxidation which they bring about. At this point there is room for still further investigation which, I believe, Winogradsky is engaged upon.

The conditions favorable to the oxidation of nitrogen compounds to nitrous and nitric acids, by the respective nitrifying organisms whose special function is to bring about these changes, have been studied extensively by Warrington, Schlösing, Winogradsky, and others, and the conditions favorable to the production of nitrates in the soil are quite thoroughly understood, and if we were able to control the meteorological conditions, it would perhaps not be a difficult matter to develop in the soil a very large quantity of nitrates suitable for plant food. As we are unable, however, to control the meteorological conditions, the best that can be done is to see that the soil is properly drained, properly cultivated, and supplied with a sufficient quantity of lime or other alkali, to prevent the acidity from interfering with the regular processes of nitrification.

Even with this, however, it has been shown by E. Breal that there may be an extensive destruction of nitrates by the action of an antagonistic bacterium or ferment, which he finds developing extensively, especially upon straw and other vegetable refuse. This ferment has the power of attacking the nitrates and liberating the nitrogen as free nitrogen. It has long since been shown that putrescent fermentation reduces nitrates to the lower oxides and finally to ammonia. This ferment, however, acts differently in that it does not reduce the nitrates to lower oxides, but sets the nitrogen free. In one case, one-third of the nitric acid under experimentation disappeared: in another, sixty-seven per cent. of the nitric nitrogen disappeared. The rapidity of the decomposition has been measured and the products of decomposition analyzed. He has shown that when the soil containing nitrates is drying, and the nitrates rising, if covered with wet straw or other vegetable refuse and allowed to dry out slowly, nitrates are not found either in the straw or surface soil. This condition, in his judgment, accounts for the failure to find nitrates in meadows, forests, or other lands strown with large amounts of vegetable refuse, a fact which was also noticed by Boussingault. It also accounts, probably, for a large amount of the loss of nitrogen which occurs when green manures are used. It is a notorious fact that a large percentage of the nitrogen stored in a crop used as a green manure seems to escape, and the discovery of this ferment by Breal probably accounts for it. We are therefore confronted by these difficulties in the production of nitrates in the soil:

(1) The reduction of nitrates by putrefactive fermentation.

(2) By the action of Breal's bacterium.

So that it seems not to be possible to produce in a soil under normal conditions, more than a very small percentage of nitrate, and rarely enough to answer the maximum requirements of a large crop.

Time will not permit me to notice the work of all of the investigators who have contributed to extend our knowledge of the activity and peculiarities of the bacteria which perform so much work for the benefit of agriculture. There is one more investigation which I wish to notice, and I am through. It is well known that there is great diversity in what is known as the availability of nitrogen in its various forms when used in compounding fertilizers, or when used as a direct fertilizer upon the land. This variation in availability is dependent upon the readiness with which the nitrogen compound, whether it be ammonia salts or vegetable or animal refuse, is converted into nitrates.

Recently, S. W. Johnson, E. H. Jenkins, and W. E. Britton, of the Connecticut Experiment Station, undertook an investigation to determine the availability of a number of the chief sources of nitrogen, used for compounding our commercial fertilizers. They used for this purpose, oats, Hungarian grass, and rye. The soil upon which the experiments were conducted was quite thoroughly exhausted by previous crops, and ordinary precautions to prevent errors creeping in were observed. They determined the percentage of available nitrogen in different sources of nitrogen, as shown by the plants indicated in pot experiments, as follows:

	Per cent.
Sodium nitrate	100.0
Dried blood	73.3
Dried fish	93.9
Ground bones	16.7
Tankage	49.4
Horn and hoof powder	63.3
Linseed meal	68.9
Cottonseed meal	64.8
Castor pumice	64.6

It will be noticed in this experiment, as is now generally the case, that sodium nitrate is taken as the standard of availability.

There is one other possible source of nitrate that may become available, and that is the nitrate that is developed by the action of electricity upon the nitrogen of the air and certain chemicals or minerals. This has not yet developed to be of economic importance, and while in the opinion of some eminent scientific men, the time may not be far distant when we may economically produce nitrate by electricity, we have not yet reached that point.

At the request of our president, I have compiled this review of the present state of our knowledge of the nitrate problem. I could not, without occupying too much of your time, go into the details of many other laborious investigations, carried on in many countries by careful and patient scientific men. What I have said is classified as follows:

(1) The sodium nitrate is the most important source from which available nitrogen can be supplied, at the present time. I have given you some account of the sources of supply, and the character and uses of the finished product as it comes into the market.

(2) The rôle that nitrate plays in agriculture.

(3) The efforts of scientific men to provide it, or furnish a substitute for it.

(4) Scientific investigations bearing upon it, showing at considerable length the important relations of bacterial life to its production and destruction.

In conclusion, I may say that science has failed, so far, to provide a substitute for the natural nitrate, and it is more economical to avail ourselves of the reserve supplies, representing the accumulated work of bacterial ferments during protracted geological periods of the past, in the now desert regions of Chili, than it is to rely upon their inadequate and uncertain work in our soils under the unfavorable natural conditions prevailing in our climate. JOHN A. MYERS.

NOTES.

On a Possible Error in the Determination of Nitrogen in Nitrates Due to Impurities in Reduced Iron.—Reduced iron is employed in two of the methods for the determination of nitrogen in nitrates, which are in use by the Association of Official Agricultural Chemists. Recently, in making blank determinations with a new lot of so-called chemically pure reduced iron it was found that, by the modified Ulsch method, much less ammonia was required for neutralizing the acid than in the case of blank tests formerly made. The error from this cause in determinations involving half a gram of commercial sodium nitrate, would amount to from 0.30 to 0.35 of a per cent. By direct distillation, without first allowing the iron to dissolve in the acid, no difficulty was experienced. The reduced iron bore the label of one of the leading manufacturers of chemicals in Germany and was ordered through a prominent and reliable firm in this country.

Since these tests were made, an account of a similar observation by L. Brandt[1] has been noticed. Brandt found in a similar manner an error equal to eight-tenths of a per cent., assuming half a gram of nitrate to be employed in a single test. As in our own case, he assured himself that the error was not due to any of the other reagents, nor to the apparatus employed, and also found that the error did not appear unless the iron was dissolved in the acid before the distillation. From various tests made by Brandt, he concluded that the impurity in the iron was in the form of some organic nitrogen compound, which probably gained access to it, subsequent to its reduction by hydrogen. Further experiments showed that the impurity could be removed by heating the iron in a current of hydrogen, though the accom-

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[1] *Chem. Ztg.*, 23, 22 (*1899*).

plishment of the object was impossible by extraction with water, alcohol, or ether. Brandt very properly closes the account of his observations by stating that the experience further indicates the propriety of never placing implicit confidence in chemicals claimed to be chemically pure, but to test everything before using it.

In view of the recent extension of the use of the modified Ulsch method in the laboratories of this country, it seemed important that our own analysts should be put on their guard as to the possible character of the reduced iron sold as chemically pure.

B. L. HARTWELL AND H. J. WHEELER.

On the Determination of Sulphur in Sulphites.—This method is founded on the following well-known reaction: Sulphur dioxide, when brought into contact with nascent oxygen and water, is transformed into sulphuric acid. The operation is conducted as follows: The weighed sulphite dissolved in water is placed in a beaker, and a mixture of water, hydrochloric acid, hydrogen peroxide, and barium chloride is added in sufficient quantity. The beaker is covered with a watch-glass, gently heated, and the operation conducted as in the case of a determination of sulphuric acid.

$$\text{Weight of } BaSO_4 \times 0.1371 = S.$$
$$\text{Weight of } BaSO_4 \times 0.2742 = SO_2.$$

The reaction comprises three phases:

(1) The sulphite is decomposed by hydrochloric acid, which liberates sulphurous acid.

(2) Sulphurous acid decomposes hydrogen peroxide and unites with the nascent oxygen forming sulphuric acid.

(3) Sulphuric acid with barium chloride gives barium sulphate.

Potassium metasulphite, $K_2S_2O_5$, analyzed by this method has given:

	Calculated. Per cent.	Found. Per cent.
Sulphur	28.8	28.8560
Potassium	35.1	34.9755
Oxygen	36.1	......

In using the bromine method the result for sulphur was 29.0202 per cent.

Commercial hydrogen peroxide cannot be employed, as it generally contains sulphuric acid. A proper reagent for this purpose is obtained by adding hydrated barium dioxide to water acidulated with hydrochloric acid.[1] The barium dioxide is added in small quantities until the liquid is alkaline, when alumina and ferric oxide are separated. The turbid alkaline liquid is thrown on a pleated filter and the filtrate collected in a vessel containing some hydrochloric acid. This filtrate is then ready for use. A. BOURGOUGNON.

Fuller's Earth.—A recent discovery of a large deposit of fuller's earth in Florida promises to be of considerable importance to the oil trade. Up to the present all the fuller's earth used by the cotton oil, and lard manufacturers has had to be imported from England and has sold for as much as $15 to $20 per ton in New York. The domestic product has so far proved unsuitable for this particular purpose and has sold for only $7 per ton, and is used only in the mineral oil industry. The product from this newly discovered deposit has been thoroughly tested by experts in the cotton oil industry and is pronounced to be fully equal to the best grades of the imported material. So soon as capital can be interested in the property the consumers will be able to obtain a high-grade fuller's earth of domestic origin which will cost them very much less than they at present have to pay. The terms on which the property is offered are so favorable that the new material will no doubt soon be put on the market.

F. T. SCHREIBER.

NEW BOOKS.

THE OUTLINES OF INDUSTRIAL CHEMISTRY. By FRANK HALL THORP, PH.D. New York: The Macmillan Co. 1898. xx + 541 pp. Price, $3.50.

While no book can fully cover a field so rich in carefully guarded secrets as those pertaining to technical chemistry, I know of no treatise on that subject which gives the student a clearer and more comprehensive view thereof than Thorp's "Outlines of Industrial Chemistry."

The student who has mastered its contents can visit a factory

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[1] This Journal, 12, No 3 (*1890*).

and, notwithstanding the usual habit of rushing the visitor through the place as quickly as possible, can understand the *modus operandi* more fully than the guide has reason to expect.

Teachers may congratulate themselves upon the appearance of this book, for it contains, expressed in a concise manner, much that would otherwise (with perhaps less happy results) require the consultation of many books.

In a work so thorough it is difficult to select any one subject more carefully treated than the others; therefore, chemists can well feel grateful to Prof. Thorp for his contribution and doubtless few libraries will be without a copy thereof.

ALFRED SPRINGER.

THE PRACTICAL COMPOUNDING OF OILS, TALLOW, AND GREASE FOR LUBRICATION, ETC. By an expert oil refiner. London: Scott, Greenwood & Co.; New York: D. Van Nostrand Co. Price, $3.50.

This book purports to give "to merchants and manufacturers in the different branches of these trades practical hints for the compounding of oils, also for the utilization of waste products, such as ullages, etc," and treats chiefly of lubricating oils, with one chapter on lamp oils.

Numerous receipts are given for compounding these oils for various uses with some hints and cautions. The flash and viscosity tests of mineral oils are described and also some of the simpler tests of animal and vegetable oils for the purpose of detecting adulteration. The real character of the various mixtures given and the reason of their usefulness for particular purposes seems to be ignored. So also the general theory of lubrication.

While to one entirely ignorant of the subject such a work would give an idea of the combinations of mineral and fatty oils which have been found useful for lubrication, it is difficult to see how the intelligent manufacturer will be benefited by so superficial a treatise. E. TWITCHELL.

LIGHTING BY ACETYLENE. GENERATORS, BURNERS, AND ELECTRIC FURNACES. BY WM. E. GIBBS, M.E. Second Edition, Revised and Enlarged. New York: D. Van Nostrand Co.; London: Crosby, Lockwood & Son. pp. 161. Illustrated. 1899. Price, $1.50.

Mention was recently made in these pages of the first edition of this work, and the present edition calls for little further notice. The author has added some twenty pages on the subject of generators, and has somewhat expanded the chapter on "Generation of Acetylene"; otherwise the volume is little changed.

A misplaced decimal point on p. 37 makes the theoretical yield of acetylene from 100 pounds of carbide 5.81 instead of 581 cubic feet. The author confuses benzine with benzene, referring to the former as a polymer of acetylene. The limits between which acetylene forms an explosive mixture with air are much greater than those stated by the author. The figures given apply more nearly to ordinary coal-gas. E. G. LOVE.

LAVAS AND SOILS OF THE HAWAIIAN ISLANDS. BY WALTER MAXWELL, Director and Chief Chemist of the Experiment Station of the Hawaiian Islands. 186 pp.

The work is an important contribution, perhaps the only contribution, to our knowledge, of the composition of the soil of the islands, which have lately come into the dominion of the United States. The total area of the islands where agriculture is possible is 6,740 square miles. The islands of the Hawaiian group are of pure volcanic origin. Fifteen volcanoes of the first class have existed at different times and been in action in the islands. The group of islands therefore represents a portion of the great mass of matter due to volcanic action, which has been projected above the water's level. The composition of the soil is, therefore, what would be expected from the decomposition of basaltic lavas. In type the soils differ from those of our country in being essentially basic instead of acidic. In the ordinary soils of the United States the acidic element, namely, silicic acid, is the predominating factor, while in Hawaiian soils, lime, alumina, and iron make up almost, if not quite, half of the total weight of the soil.

In the decay of these lavas, in the activity of the usual forces which produce the disintegration of rocks, the functions of water, steam, and air have been extremely prominent. In addition to this the vapors of sulphuric acid, which find their way by means of the steam into the crevices and broken surfaces of the lava masses, has added greatly to the power of water and steam in disintegrating the rock masses. In one instance where a quantity of steam was condensed and preserved for analysis, it was found to contain 4.92 per cent. of sulphuric acid. The steam contains practically no chlorine, which leads to the belief that the sea-waters do not penetrate into the depths whence the heat of the volcanoes comes.

Two distinct types of soils have arisen from the decay of these volcanic lavas. These are distinguished chiefly by their color and are known as the "yellow" and "red soils." In regard to fertility the dark red soils are much more productive than the light red or yellow soils.

The Hawaiian soils are remarkably rich in phosphoric acid and in iron, about twenty-five per cent. of the weight of the soil consisting of iron oxide. Thus it is seen that the silica of American soils is largely replaced by the iron and aluminum of Hawaiian soils.

The chief agricultural crop of the Hawaiian Islands, as is well known, is sugar, and there is no country in the world where so great a quantity of sugar can be grown per acre. In general, it requires two years to produce one crop, inasmuch as the crop is allowed to grow about eighteen months, and the other six months are consumed in harvesting, preparing the lands, and replanting.

The average yield of sugar, per acre, for the "dark red soils" is a little over 10,000 pounds, and for the "yellow soils" a little over 6,000 pounds. Very much larger yields are occasionally reported; namely, from 20,000 to 25,000 pounds per acre in some instances.

In the methods of analysis for determining the available plant food in soils, Dr. Maxwell has introduced an interesting innovation. He has proposed the use of aspartic acid, as a solvent for the available plant food in soils; namely, the phosphoric acid and the potash.

In a comparison of the amount of plant food removed by successive cropping with sugar-cane and that removed by digestion with a one per cent. solution of aspartic acid for twenty-four hours, he has shown that in ten years of cropping practically the same quantity of plant food is removed, as in the digestion of the soil for twenty-four hours with a one per cent. solution of aspartic acid. He therefore proposes to measure the available plant food present in the soil by digesting with a one per cent. solution of aspartic acid for twenty-four hours and dividing by ten the quantity of phosphoric acid and potash obtained.

Under the conditions of rainfall, which prevail in the parts of the islands studied by Dr. Maxwell, he has found that the quantity of plant food removed by cropping is practically the same as that removed by the drainage waters.

The student of soil chemistry and physics as well as the practical farmer will derive much benefit by carefully reading Dr. Maxwell's pamphlet. H. W. WILEY.

TESTING MILK AND ITS PRODUCTS. BY E. H. FARRINGTON AND F. W. WOLL. Fourth revised and enlarged edition. Madison, Wis.: Mendota Book Company. viii + 256 pp.

The general introduction of the Babcock method has been one of the most important aids to the producer of dairy products, and as a natural result, there has been a demand for a work which would enable one to understand and apply the processes connected with modern dairy practice. This demand has been met by the authors in an admirable little volume upon the subject which is now in its fourth edition. Consideration is given to the principles of the Babcock method, followed by many aids and apt suggestions in order that one may become familiar with the method and its application. The testing of milk is treated in a thorough manner and especially is the treatment of the methods for the determination of the acidity of milk and cream to be recommended. The chemical analysis of dairy products is a section of the work which is of interest to the chemist as well as to one who has not had the advantage of laboratory training. The appendix contains many useful tables and helpful suggestions on practical creamery work. A very complete index closes the volume. The volume, as a whole, is a helpful one, and should be in the hands of those interested in the application of improved methods in the dairy industry of the country.

J. B. WEEMS.

BOOKS RECEIVED.

Digestion Experiments. Bulletin No. 160. The North Carolina Agricultural Experiment Station, Raleigh, N. C. 20 pp.

Drinking Water—City, Town, and Rural Supplies. Bulletin No. 161. The North Carolina Agricultural Experiment Station, Raleigh, N. C. 20 pp.

Farmers' Bulletin No. 87 (Experiment Station Work, VIII), U. S. Department of Agriculture, Washington, D. C. Soil Moisture; Fertility of Soils; Clover Crops for Orchards; Cultivating vs. Cropping Orchards; Transplanting Trees; Fecundity of Swine; Food Value of Eggs; Starch from Sweet Potatoes; The Toad as a Friend of the Farmer. 1899. 32 pp.

Commercial Fertilizers. By J. H. Stewart and B. H. Hite. Bulletin No. 53. West Virginia Agricultural Experiment Station, Morgantown, W. Va. December 31, 1898. 32 pp.

A Select Bibliography of Chemistry, 1492–1897. By Henry Carrington Bolton. First Supplement. City of Washington: Published by the Smithsonian Institution. 1899. vii + 489 pp.

The Spirit of Organic Chemistry. An Introduction to the Current Literature of the Subject. By Arthur Lachman and Paul C. Freer. New York: The Macmillan Co. 1899. xii + 229 pp. Price, $1.50.

Manurial Requirements of Crops. Bulletin No. 58. Hatch Experiment Station of the Massachusetts Agricultural College. March, 1899. Amherst, Mass. Press of Carpenter & Morehouse, 1899.

The British Food Journal and Analytical Review. The Official Organ of the International Commission on Adulteration. Published Monthly. First number issued January, 1899. Subscriptions received by P. Blakiston's Son & Co., Agents for America, 1012 Walnut St., Philadelphia. Price, $2.00 a year.

The Alkali Soils of the Yellowstone Valley from a Preliminary Investigation of the Soils near Billings, Montana. By Milton Whitney and Thomas H. Means. Bulletin No. 14. U. S. Department of Agriculture, Division of Soils. Washington, D. C.: Government Printing Office. 1898. 39 pp.

The Arithmetic of Chemistry, being a simple treatment of the subject of chemical calculations. By John Waddell. New York: The Macmillan Co. viii + 137 pp. Price, 90 cents.

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Drinking Water. Bulletin No. 161. The North Carolina Agricultural Experiment Station, Raleigh, N. C. January 31, 1899. 20 pp.

The United States at the Paris Exposition in 1900. By Ferdinand W. Peck, Commissioner General for the United States to the Paris Exposition of 1900. A Reprint from the North American Review. January, 1899. 11 pp.

General Information for Citizens of the United States of America who Desire to Become Exhibitors at the International Exhibition Universelle. Paris, 1900. Regulations classified. January, 1899. 110 pp.

A Treatise on Photographic Optics. By R. S. Cole, M.A. New York: D. Van Nostrand Co. 1899. 330 pp. Price, $2.50.

I. The Raspberry Saw-fly. II. Preliminary Notes on the Grape Vine Flea Beetle.—Bulletin No. 150. Experiments in Ringing Grape Vines.—Bulletin No. 151. Two Destructive Orchard Insects.—Bulletin No. 152. Director's Report for 1898.—Bulletin No. 153. Commercial Fertilizers for Potatoes (II).—Bulletin No. 154. New York Agricultural Experiment Station, Geneva, N. Y. 100 pp.

U. S. Department of Agriculture, Library Bulletin. February, 1899. Washington, D. C. 24 pp.

Practical Materia Medica for Nurses, with an appendix containing poisons and their antedotes, with poison emergencies, mineral waters, weights and measures, dose list, and a glossary of the terms used in materia medica and therapeutics. By Emily A. M. Stoney, Philadelphia: W. B. Saunders (925 Walnut St.). 1899. 306 pp.

Insecticides, Fungicides, and Spraying Calendar. Bulletin No. 60. Hatch Experiment Station of the Massachusetts Agricultural College, Amherst, Mass. April, 1899. 10 pp.

Eleventh Annual Report of the Agricultural Experiment Station, University of Illinois, 1897–98. Urbana, Illinois. 15 pp.

Spraying Apple Trees, with Special Reference to Apple Scab Fungus. Bulletin No. 54. Agricultural Experiment Station of the University of Illinois. Urbana, Ill. 24 pp.

VOL. XXI. [JUNE, 1899]. No. 6.

THE JOURNAL

OF THE

AMERICAN CHEMICAL SOCIETY.

EGG ALBUMIN.

BY THOMAS B. OSBORNE.

Received May 18, 1899.

HOPKINS has recently shown[1] that the crystallization of egg albumin is greatly facilitated by the addition of acetic acid to the half saturated ammonium sulphate solution. I have found that crystallization is thus promoted, because the crystallized egg albumin is a compound of the protein substance with acid.

When egg white is first mixed with half saturated ammonium sulphate solution an alkaline reaction towards litmus can be detected and a decided odor of free ammonia develops. After this solution has stood for some hours, all evidence of free ammonia disappears and the solution is then perfectly neutral to litmus and continues neutral during the gradual separation of the albumin. The deposited substance, whether in the form of spheroids or of crystals, when filtered out and dissolved in water, reacts distinctly acid with litmus, as well as with phenolphthalein.

In order to obtain the albumin in crystals, it has heretofore been necessary to precipitate it several times, evidently because, during the earlier evaporations, an insufficient amount of acid

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[1] *Jour. Physiology*, 23, 131.

is formed to produce the crystalline compound. It is also for this reason that, if acetic acid be added as Hopkins directs, the albumin is obtained completely crystallized by a single precipitation, and that too without any concentration by evaporation.

I have found that if, instead of acetic acid, a molecularly equivalent quantity of hydrochloric acid be added, the separation takes place even more quickly and, so far as my experience has as yet gone, within a short time is more complete than with acetic acid during the same time. Thus, I prepared from two portions of 1500 cc. each of perfectly fresh egg white a quantity of crystallized egg albumin by aid of each of these acids, with the following results:

After adding to one-half of the egg white, acetic acid in the proportion and manner directed by Hopkins, and a molecularly equivalent quantity of hydrochloric acid mixed with 300 cc. of half-saturated ammonium sulphate solution to the other half, the two solutions were set aside to deposit albumin. After three hours a very large crystalline precipitate had separated in the portion with hydrochloric acid. This precipitate was then filtered out, but the portion with acetic acid was allowed to stand for twenty-four hours, because the separation appeared to be much less than that in the hydrochloric solution.

These two precipitates were each twice recrystallized, freed as completely as possible from mother-liquor, by pressing out with filter-paper, dissolved in water, and the solutions dialyzed for ten days, until wholly freed from sulphate, when they were filtered clear and evaporated at about 50°. The residue left by the acetic acid solution, A.1, weighed twenty-nine grams; that from the hydrochloric acid, H.1, fifty-nine grams.

The filtrates from the several crystallizations of these two preparations yielded a second crop of completely crystallized albumin; that from the acetic acid solution, A.2, weighing forty-three grams; that from the hydrochloric acid solution, H.2, seven and nine-tenths grams. Similarly, from the mother-liquors from these preparations, two other entirely crystalline products were obtained, weighing respectively, A.3, eight grams and H.3, four and nine-tenths grams. From the finally remaining acetic acid solutions another preparation separated, consisting wholly of spheroids, A.4, which weighed nine and one-tenth grams.

There were thus secured from 1500 cc. of egg white, by adding acetic acid, 80 grams of wholly crystallized albumin, and from 1500 cc., with hydrochloric acid, 73.2 grams, or 5.30 and 4.90 grams respectively per cubic centimeter of egg white.

The crystallized albumin, like all the other protein preparations which I have as yet examined, is a compound of a protein substance with an acid. In order to neutralize to litmus and to phenolphthalein the solutions of one gram of each of these preparations of albumin, it was necessary to add the following quantities of decinormal potassium hydroxide solution:

	A.1.	A.2.	A.3.	A 4.	H.1.	H.2.	H.3.
To phenolphthalein·····	2.05	2.30	2.30	2.35	2.05	2.25	2.20
To litmus···············	1.30	1.60	1.65	1.55	1.30	1.60	1.50
Difference··············	0.75	0.70	0.65	0.80	0.75	0.65	0.70

If, as pointed out in another paper, the molecular weight of the protein substance is about 15,000,[1] one gram would react with 0.67 cc. of a decinormal solution. a quantity nearly equal to the difference in acidity shown by these two indicators. Three molecules of acid reacting with one of albumin would be equal to two cc. of decinormal solution per gram of albumin, a quantity in very close agreement with that found for the two fractions constituting the greater part of all the albumin, A.1, and H.1., and which also differs but little from that required to neutralize one gram of all the other fractions.

When the albumin, dissolved in water, was neutralized with decinormal potassium hydroxide, the solution evaporated to dryness and the proteid matter burned off, an ash was left containing potassium carbonate almost molecularly equivalent to the acid of the albumin originally neutralized. From this it appears that the acid is mostly, if not wholly, organic.

It has been, thus far, impossible to discover what acid or acids were united to the albumin. Neutralization of the albumin suspended in fifty per cent. alcohol resulted in the formation of a gummy mass difficult to filter and wash, and from which none of the products of neutralization could be separated. Neutralization of a solution of ten grams of the albumin and dialysis in distilled water, failed to give enough salts in the diffusate to shed light on the nature of the acid. Neutralization with baryta of a

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[1] Sabanejeff: *Chem. Centrbl.* (*1891*), 10, found the molecular weight of purified egg albumin by determining the lowering of the freezing-point to be 15,000.

solution of two grams of the albumin gave a very slight precipitate, which after standing some days, was filtered out, washed and ignited, but only four milligrams of mineral matter were obtained.

The preparations showed no excess of sulphur over that usually found in coagulated and thoroughly washed albumin prepared without the use of sulphuric acid or sulphates. Determination of total phosphorus showed A.1 and H.1 to contain 0.38 and 0.40 per cent. phosphorus pentoxide respectively. These preparations contained 0.87 and 0.69 per cent. of ash which was almost wholly insoluble in water and appeared to consist chiefly of calcium phosphate. The total phosphorus in these preparations was equal to 0.59 and 0.64 per cent. of tricalcium phosphate respectively.

Towards lacmoid these preparations reacted alkaline, about one cc. of decinormal acid being required to neutralize the solution of one gram, and three cc. to give an acid reaction. When one gram was treated with decinormal hydrochloric acid, no evidence of free acid was shown with tropæolin, until eight or nine cc. were added.

When pure water solutions containing two and five-tenths per cent. of my albumin preparations were heated they all became turbid at 58°–59° and separated a minute quantity of flocks at 59°–60°. On gradually raising the temperature the coagulum slowly increased until at 70° much of the dissolved albumin had coagulated. The solutions heated for some time at 74° and filtered still contained a little proteid which even on heating at 99° did not separate until some salt was added. No break in this gradual coagulation of the albumin was detected, the solutions when filtered after partial coagulation yielding a coagulum on again heating up to the temperature to which they had been developed at previously heated.

When solutions of pure ten per cent. sodium chloride brine containing two and one-half per cent. of each of these preparations except A.3, H.3 and A.4 were slowly heated, turbidity developed at 56°–59° and flocks at 56°–60°.

Only a trace of coagulum was obtained, however, below 64°, and the solutions filtered from this remained perfectly clear until heated to nearly or quite 70°, when the albumin began to coagulate. It was, however, found necessary to heat the solution to nearly 84° before most of it was separated.

The three preparations A.3, H.3, and A.4, behaved as just described, except that below 64° each yielded a relatively considerable coagulum. These preparations, it is to be noted, are final fractions obtained in small quantity and it seems probable that this coagulum obtained at 60°–64° is due to the presence of a different substance from that constituting the chief part of the other fractions. This is the more probable as A.3 and A.4 also showed a difference in specific rotation, as well as in composition.

The degree of acidity was found to have much influence on the coagulation of the albumin. Exact neutralization to phenolphthalein, as might be expected, entirely prevented coagulation, even on boiling. When the acid of the albumin was neutralized so that the acidity was equal to one and two-tenths cc. of decinormal solution per gram of albumin, a solution containing two and five-tenths per cent. of the proteid became slightly opalescent on heating to 72° and remained otherwise unchanged, even after heating for a long time in a boiling water-bath. If, however, the acidity was but one-tenth cc. greater, that is, equal to one and three-tenths cc. per gram of albumin, the solution became turbid at 70°, and very opaque after heating in the water-bath at 99°. The difference between the two solutions was marked and it is evident that the additional one-tenth cc. had caused a change in the condition of the albumin. An acidity of 1.33 cc. per gram is almost exactly equal to two molecules of acid per molecule of albumin, assuming the latter to have a molecular weight of 15,000. From this it would seem to be necessary to add three molecules of acid to one of albumin, in order to form the coagulable substance.

The specific rotation of these preparations was approximately determined by means of a Schmidt and Haensch polarimeter using a 200 mm. tube. The readings on the sugar scale were converted into degrees of circular polarization by multiplying by 0.346. The formula used in calculating the results was

$$(a)_D = \frac{a \times 100}{p \times d \times l} \text{ where}$$

a = observed rotation,
p = per cent. of albumin in the solution,
d = density of the solution,
l = length of tube in decimeters.

The results obtained were as follows:

Preparation.	Per cent. of dissolved albumin.	Solvent.	Rotation.	Average.
A.1	5.861	Water	−29° 48′	−29° 17′
	6.670	"	−28° 46′	
A.2	3.422	"		−29° 23′
A.3	3.273	"		−33° 3′
A.4	3.404	"		−41° 45′
H.1	3.425	10 per cent. NaCl	−29° 0′	−28° 35′
	3.237	Water	−28° 33′	
	6.478	"	−28° 1′	
H.2	1.699	"		−28° 14′
H.3	3.205	"		−39° 31

As the results obtained on A.1, A.2, H.1, and H.2, agree closely and as these preparations represent very different proportions of the total albumin of the egg white, it seems probable that we have in these fractions but one substance.

Bondzynski and Zoja, working with solutions containing ammonium sulphate, obtained similar but somewhat lower figures for the specific rotation of their least soluble fractions; namely, 25° 8′ and 26° 2′, duplicate determinations on the same fraction. Two other fractions gave them 34° 18′ and 42° 54′, figures agreeing fairly with those obtained by me for my more soluble fractions. They determined the albumin in the polarized solution by coagulation, a process which does not admit of so exact a determination of the dissolved albumin as that employed by me, which consisted simply in evaporating the pure water solution to dryness, drying to constant weight at 110° and deducting ash. A slight error in determining the dissolved albumin causes a considerable error in the specific rotation.

The effect of acid and alkali on the rotation of the albumin solutions is shown by the following results, obtained by dissolving one gram of A.2, in twenty-five cc. of water and treating with the given quantities of acid or of alkali:

1 gram A.2 + nothing		−29° 17′
+ 0.8 cc.	N/10 HCl	−29° 5′
+ 8.0 cc.	"	−33° 46′
+ 1.4 cc.	N/10 KOH	−28° 45′
+ 2.7 cc.	"	−30° 20′
+ 4.2 cc.	"	−32° 30′

It is to be noted that by eight cc. of the acid and by four and two-tenths cc. of the alkali a rotation was produced about ten per cent. higher than with the smaller quantities of acid or alkali. This increase may well be due to a local overreaction taking place on mixing the acid and alkali with the proteid solution, it having been demonstrated that large proportions of acids and alkalies yield products of high specific rotation.

Panormoff[1] has studied the specific rotation of fractionally precipitated crystallized egg albumin and concludes that there are two albumins present in egg white, one with a specific rotation of —23.6° and the other —46.2°. The albumin with the lower rotations he obtains from the so-called egg globulin precipitated by adding an equal volume of saturated ammonium sulphate solution to the egg white. This he succeeded in crystallizing and, so prepared, finds it to have the properties and composition of albumin. He considers, therefore, the egg globulin to be a compound of egg albumin with some unknown substance.

As the egg white is alkaline to litmus and ammonia is set free on adding to it a saturated solution of ammonium sulphate, it is not surprising that a product should be produced of different solubility from that of the albumins which we have been considering.

Panormoff converted his crystallized albumin into a chloride by dialysis against two-tenths per cent. hydrochloric acid. He analyzed the product obtained and it is interesting to note that, if calculated free from hydrochloric acid, the figures for the albumin are in exceedingly close agreement with the average of the best analyses of albumin. Furthermore, the proportion of hydrochloric acid in the compound is exactly the same as that which I found with tropæolin to be fixed by the albumin; that is, I found that one gram of albumin united with eight cc. of decinormal acid or 0.0292 hydrochloric acid to form a compound showing no free acid with tropæolin, while Panormoff's chloride contained 2.92 per cent. or exactly the same quantity.

In regard to the composition of egg albumin, confusion has recently been caused by Hofmeister, who states[2] that he has found in repeatedly crystallized egg albumin 1.01 and 1.18 per cent. of sulphur and that Dr. F. N. Schulz, in his laboratory, has obtained 1.24 and 1.27 per cent. He consequently calls in ques-

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[1] Ref. in *Chem. Centrbl.* (*1898*), II, 358 and 487.

[2] *Ztschr. physiol. Chem.*, 24, 166.

tion the purity of the samples of crystallized albumin, analyzed with great care by Bondzynski and Zoja. As Hofmeister's figures for carbon are higher and for nitrogen lower than those of Bondzynski and Zoja, as well as of other investigators who have analyzed *amorphous* egg albumin, the whole question of the composition of this substance is again thrown into confusion.

Having at hand a sample of egg albumin, which had been three times recrystallized in the manner described by Hofmeister as necessary for its purification, and obtained in the same proportion from the egg white as stated by him to be the usual yield after thorough purification, and which had been coagulated with alcohol and thoroughly washed until all the ammonium sulphate had been removed, I analyzed it, dried at 110°, with the result given under No. 1.

Analyses of the seven fractionally crystallized preparations A.1-4, and H.1-3, were made after drying them to constant weight at 110°.

	No. 1.	H.1.	H.2.	H.3.
Carbon	52.18	52.85	52.33	51.72
Hydrogen	6.91	6.92	6.90	6.90
Nitrogen	15.67	15.66	15.77	15.26
Sulphur	1.70	1.572	1.644	1.958
Oxygen	23.54	22.998	23.356	24.162
	100.00	100.00	100.00	100.000
Ash	0.56	0.69	0.67	0.59
Total phosphorus pentoxide	....	0.40	0.21	trace

	A.1.	A.2.	A.3.	A.4.
Carbon	52.60	52.61	52.33	51.44
Hydrogen	7.02	6.94	6.93	6.88
Nitrogen	15.54	15.76	15.40	15.20
Sulphur	1.610	1.612	1.778	1.912
Oxygen	23.230	23.078	23.562	24.568
	100.000	100.000	100.000	100.000
Ash	0.87	0.65	0.67	0.40
Total phosphorus pentoxide	0.37	0.28	trace	trace

There can no longer be question about the amount of sulphur in albumin being greater than that stated by Hofmeister. My sulphur determinations were made with extreme care, fusing more than a gram of the substance over an alcohol lamp with pure sodium hydrate and peroxide in a nickel crucible,[1] dissolving the fusion in an excess of hydrochloric acid, neutralizing most of the excess of acid and precipitating with barium chloride from a boiling solution of at least 800 cc. volume. Blank determinations showed no trace of sulphur in the reagents and also that none was absorbed during the fusion over the alcohol lamp. These results agree with those obtained by Bondzynski and Zoja, though the difference in composition between their extreme fractions was not quite so great as found for my preparations.

The composition, rotation, heat-coagulation points and reactions of the crystallized egg albumin obtained by aid of hydrochloric or acetic acids show this to be the same substance as that which has in the past been regarded as egg albumin.

My results, those of Bondzynski and Zoja, and of Panormoff, make it plain that there are two protein substances in the egg white, which are commonly obtained admixed when preparing egg albumin by the usual processes. Whether the extremes of my fractional precipitations of these two albumins consist wholly or even largely of each one of these bodies requires further investigation of large quantities of egg white. This work we now have well under way.

Moerner[2] has described ovomucoid as identical with Neumeister's pseudopeptone,[3] and states that it constitutes about one-eighth of the organic substance of the egg white. As this substance is described as largely, though not wholly, precipitated by two-thirds saturation of its solution with ammonium sulphate, it ought, if present as such in the egg white, to be found among the more soluble fractions thrown down by successive additions of ammonium sulphate. It is intended to direct especial attention to the isolation of this substance and to determine if possible in how far it may be admixed with the albumins.

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[1] I have found many times when using a nickel crucible that, on dissolving the fusion, there was a black substance present (this looks and behaves like nickel sulphide, but it seems hardly possible that nickel sulphide could escape oxidation), which, when filtered out and oxidized, was found to contain sulphur. This black substance should be dissolved by the chlorine liberated from the hydrochloric acid by the peroxide of hydrogen, otherwise too low results will be obtained.

[2] *Ztschr. physiol. Chem.*, 18, 525.

[3] *Ztschr. Biologie*, 9, 369.

ON SOME DEFINITE COMPOUNDS OF PROTEIN-BODIES.

BY THOMAS B. OSBORNE.

Received May 18, 1899.

PROTEIN-BODIES, as hitherto prepared in a state fit for the study of their composition and properties, are commonly considered to be, for the most part, distinct organic molecules, not united to either acids or bases.

Although protein-bodies are known to combine or react with acids, bases and halogens, scarcely any of their compounds or derivatives have been as yet described of constant or definite composition, except in cases where the original substance has been profoundly modified or broken up.

The object of this notice is to state briefly some results of an investigation which leads to the conclusion that protein-bodies, as hitherto prepared, are, in fact, definite chemical compounds of protein-substance with common mineral acids, or contain such compounds in admixture.

A large number of the purest protein-preparations that it has hitherto been possible to make in this laboratory, including egg albumin several times recrystallized, edestin, legumin, excelsin, amandin, corylin, phaseolin, gliadin, hordein and zein,[1] are, without exception, acid to phenolphthalein, slightly acid or neutral to litmus and decidely alkaline to lacmoid.

To render gram portions of the above-named substances neutral to litmus has required in some cases not any, in others from one-tenth cc. to one cc., and in a very few instances a little more than one cc. of decinormal alkali solution. To make the same gram portions neutral to phenolphthalein, a further quantity of about one cc. of decinormal alkali has been required, except for legumin, which took up about two cc.

By help of lacmoid and other indicators, it can be shown that these protein-bodies are able to combine with additional quantities of acids.

In case of edestin preparations,[2] that had been deposited from

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[1] See papers by the author and his associates in *Am. Chem. J.*, 13, 14 and 15. This Journal, 16, 17, 18, 19, and 20. Also Griessmayer, Die Protiede, etc., Heidelberg, 1897.

[2] Edestin is one of several crystallized substances which are frequently termed plant-vitellin. It was first prepared by Barbieri from squash seeds, and was obtained in distinct crystals by Grübler. It was afterwards extracted from seeds of hemp, castor bean and sunflower, by Ritthausen. (*J. prakt. Chem.*, (2) 18, 102; 23, 97 and 481.) The author and his associates have identified it in the seeds of flax, cotton, wheat, rye, barley, and maize. See also *Am. Chem. J.*, 14, 671; this Journal, 18, 609.

salt solutions, I have undertaken to determine what acids are present which thus react with an alkali.

When such an edestin preparation is suspended in water and made neutral to phenolphthalein, edestin itself, pure and simple, remains undissolved, while the added alkali carries into solution its equivalent of the acid or acids which had been united to the edestin.

What acids are thus removed from edestin depends upon the conditions of its preparation, that acid being predominant which was most abundant as a mineral salt in the solution from which the edestin last separated.

Accordingly, edestin that has been precipitated from sodium chloride brines carries with it hydrochloric acid chiefly, but, when thrown down from ammonium sulphate solutions, it is united to sulphuric acid. It appears to be also in small part combined to an organic acid, as yet unidentified, whose alkali salt yields carbonate when ignited.

The smallest quantities of alkali carbonate and, therefore, it is to be inferred of organic acid, have come from those preparations which have been repeatedly deposited out of sodium chloride brine.

The solutions hitherto obtained on thus neutralizing edestin preparations with alkali, have invariably contained a very little organic matter which when strongly heated gives out a peculiar characteristic odor and yields alkaline vapors.

Property of Edestin.—Before giving further account of edestin compounds, it is best to state explicitly some of the characters of edestin itself.

As before mentioned, when preparations which contain edestin chemically united to acids are suspended in a little water and made exactly neutral to phenolphthalein by addition of dilute solution of potassium hydroxide, the edestin remains undissolved, and after washing with pure water is, so far as we have been able to discover, entirely free from the acids that were combined with it.

Thus isolated edestin is insoluble in pure water, but dissolves readily in decinormal alkali and also in decinormal hydrochloric acid. Of the alkali seven-tenths cc. and of the acid one and four-tenths cc. are required to effect the solution of one gram of water-free edestin.

Pure edestin dissolves freely in a ten per cent. brine of pure sodium chloride. This solution, freshly prepared, is neutral to phenolphthalein, but alkaline to litmus and strongly alkaline to lacmoid. When this solution is heated to 99° in a boiling water-bath, it is very slowly and imperfectly coagulated.

Solution of edestin in ten per cent. brine, when saturated with sodium chloride, is precipitated slightly; when saturated with magnesium sulphate, it is precipitated more largely, and on saturating with sodium sulphate at 34°, the edestin is thrown down completely.

EDESTIN HYDROCHLORATES.

Monohydrochlorate.—If pure edestin, neutral to phenolphthalein, be dissolved in ten per cent. sodium chloride brine and gradually mixed with an equal volume of the same brine containing one cc. of decinormal hydrochloric acid for each gram of edestin, a nearly or quite clear solution is obtained, which, when dialyzed, yields a wholly crystalline deposit. On washing with water a part of this deposit dissolves after the salts have been removed, and a part remains undissolved being wholly insoluble in water. This latter substance is edestin monohydrochlorate.

When dissolved in brine, one gram of this salt is neutralized to phenolphthalein by seven-tenths cc. of decinormal alkali solution. Assuming that edestin has a molecular weight of about 14,300,[1] this body, insoluble in water, consists of one

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[1] The simplest formula for edestin (containing two atoms of sulphur) which can be calculated from the average of a large number of closely agreeing analyses (carbon, 51.55; hydrogen, 6.92; nitrogen, 18.67; sulphur, 0.90; oxygen, 21.96) gives a molecular weight of 7,138, twice which is 14,276, the formula being, carbon, 614; hydrogen, 988; nitrogen, 190; sulphur, 4; oxygen, 196.

Calculation of similar formulas for plant globulins containing but four-tenths per cent. of sulphur shows that these substances, if there are two atoms of sulphur in the molecule, must have a molecular weight of not less than 14,500. The same is true for globin from oxyhaemoglobin recently analyzed by Schultz. Closely agreeing molecular weights for the more carefully analyzed protein-bodies can be calculated from their analyses by multiplying the simplest formula containing one atom of sulphur by such a factor that each formula shall contain two or more atoms of sulphur and have a molecular weight nearest to 15,000. For twenty-seven distinct protein-bodies of vegetable and animal origin formulas strikingly similar to that above given for edestin are so obtained, and also molecular weights, nearly all of which are very nearly 15,000, the extremes being 14,068 and 16,074. Those protein substances known to be compound bodies, like oxyhaemoglobin and casein, give higher molecular weights. The number of sulphur atoms in these formulas ranges from two to ten. One gram of substance having a molecular weight of 15,000 would require for a complete molecular reaction 0.66 cc. of a decinormal solution.

molecule of edestin combined with one molecule of hydrochloric acid.

When pure edestin is dissolved in ten per cent. neutral sodium chloride brine and the solution, which is neutral to phenolphthalein, is dialyzed, imperfectly developed crystals are deposited that, when dissolved in neutral brine, yield a solution having an acidity nearly or quite equal to that of edestin monohydrochlorate.

Edestin monohydrochlorate is wholly insoluble in water, but dissolves in ten per cent. sodium chloride brine to a solution from which it is readily thrown down by adding water. On warming the thus diluted brine, the precipitate dissolves and reappears on cooling in octahedral crystals.

A solution containing five per cent. of edestin monohydrochlorate and ten per cent. of sodium chloride becomes turbid when heated to 95°, and a flocculent coagulum separates slowly on continued heating at 99°.

Edestin Bihydrochlorate.—When pure edestin is treated with insufficient dilute hydrochloric acid to dissolve it all, the part dissolved consists of bihydrochlorate of edestin. To neutralize to phenolphthalein one gram of edestin thus dissolved, one and one-fourth cc. of decinormal alkali are required, and in the solution from which edestin is thereby precipitated, alkali chloride is formed very nearly equivalent to the alkali added.

Edestin bihydrochlorate is soluble in pure water, its solution therein being, however, precipitated by very small quantities of alkali salts. Although quite insoluble in one or two per cent. sodium chloride brine, edestin bihydrochlorate freely dissolves in ten per cent. salt solution.

From ten per cent. sodium chloride brine the bihydrochlorate separates on dialysis in octahedral crystals. By diluting its solution in ten per cent. brine a precipitate is formed, which dissolves on warming the diluted brine. On cooling, this solution deposits the substance in very perfect crystals.

The ten per cent. sodium chloride solution of edestin bihydrochlorate, like the similar solutions of the monohydrochlorate and of edestin, gives, when saturated with sodium chloride, a very slight precipitate; when saturated with magnesium sulphate, somewhat more, and saturated at 34° with sodium sulphate is completely precipitated.

A solution containing ten per cent. of sodium chloride and ten per cent. of edestin bihydrochlorate gives a slight precipitate when mixed with one-half its volume of water, and a rapidly increasing precipitate on continued dilution.

A solution containing ten per cent. of sodium chloride and five per cent. edestin bihydrochlorate gives a slight precipitate with an equal volume of water. When heated in a double water-bath, ten per cent. salt solution containing five per cent. of edestin bihydrochlorate becomes turbid at 90° and at 91° flocks separate, which gradually increase in quantity on heating at 99°. Edestin bihydrochlorate dissolved in water or salt solution reacts acid to phenolphthalein and litmus, but is strongly alkaline to lacmoid.

When the solution of edestin bihydrochlorate in water is made neutral to phenolphthalein, by addition of alkali, the edestin separates out completely and is then almost entirely soluble in ten per cent. brine.

From the water solution of edestin bihydrochlorate the edestin is completely thrown down by small quantities of soluble salts; but this precipitate is not wholly redissolved by ten per cent. brine, a relatively small portion remaining insoluble, which is more acid than edestin bihydrochlorate while the substance redissolved is less acid and shows the properties of a mixture of the mono- and bihydrochlorate.

OTHER ACID SALTS OR DERIVATIVES OF EDESTIN.

1. The substance insoluble in ten per cent. solution of sodium chloride, last mentioned in the preceding paragraph, is or contains a third more acid compound or derivative of edestin, which on neutralization yields a product wholly different from edestin, which is now under investigation. Its study is expected to throw light on the nature of "acid albumin" and of Weyl's "albuminate."

2. All edestin preparations, obtained from sodium chloride extracts of hemp-seed by dialysis or by cooling, when dissolved in a minimum of hydrochloric acid, react so strongly alkaline

with lacmoid[1] that a total of from two and five-tenths to three cc. of decinormal acid are required to neutralize to lacmoid the solution of one gram of edestin, and to obtain an acid reaction with this indicator a total of about eleven cc. of acid per gram are necessary.

3. On treating several gram portions of edestin with uniformly increasing quantities of decinormal hydrochloric acid and testing for free acid with mixed potassium nitrite, iodide and starch paste, a very marked difference was seen in the intensity of the reaction, between six and five-tenths cc. of decinormal acid per gram or less, and seven cc. or more, strongly indicating a firmer binding of the smaller quantity of acid.

4. With tropæolin no reaction for free hydrochloric acid could be obtained until thirteen cc. of decinormal acid had been added, a quantity just twice that found in testing for free acid with potassium nitrite.

Closely agreeing figures are given by this indicator, and different preparations of the same protein body have given accordant results; thus, three different samples of edestin reacted with 12.9 cc., 12.5 cc, and 12.7 cc.

Many other protein preparations thus tested have shown that from nine to thirteen cc. of acid are bound by one gram of substance. Excelsin fixed 12.4 cc.; legumin from three different seeds fixed 12.5 cc., 12.9 cc., and 13.4 cc.; amandin took up 10.3 cc. and crystallized egg albumin 9 cc.

Whether the results of the interaction of edestin with these larger quantities of hydrochloric acid are simply edestin salts, or products of its decomposition or alteration. is as yet undetermined.

Edestin forms soluble compounds with nitric and acetic acid in the same molecular proportions as with hydrochloric acid.

When former edestin preparations (separated from salt solution by dialysis), which yield on neutralization chlorides, sulphates, in some cases traces of phosphates, and always more or less organic matter, are suspended in water and treated with measured amounts of hydrochloric acid (not in excess), they dissolve in proportion to the quantity of acid added, provided the amounts of water-soluble substance (bi-acid edestin) orig-

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[1] Blood, milk and other animal fluids, as well as saline extracts of seeds, react strongly alkaline with lacmoid. This reaction, though doubtless due to some extent to alkaline phosphates, is unquestionably chiefly caused by the protein constituents of the fluid.

inally contained in the preparations be deducted from the total quantities dissolved. Thus, several series of determinations of the solubility of edestin were made by suspending gram portions in water enough to make a final volume of twenty cc. and adding successively increasing quantities of centinormal hydrochloric acid. After frequently shaking during several hours, the solutions were allowed to settle, filtered clear, the acidity to phenolphthalein determined, the solutions evaporated, the residues dried at 110° and weighed.

It was found that the amount of edestin thus dissolved increases quite uniformly with increased quantity of acid, and that a little over 0.11 gram of the substance is carried into solution by each additional cc. of centinormal hydrochloric acid. The acidity of the soluble body thus produced is very nearly that of a compound of edestin with two molecules of monobasic acid.

Those preparations which yield relatively much alkali sulphate on neutralization are less soluble in hydrochloric acid than the others, and the water-soluble edestin compounds resulting are relatively more acid, since pure edestin requires for solution more sulphuric than hydrochloric acid, and the soluble edestin sulphates are much more acid than the soluble bihydrochlorate. All the preparations of edestin whose solubility in hydrochloric acid we have determined yield more or less alkali sulphate on neutralization. To this fact we attribute the slightly less degree of solubility in hydrochloric acid found than that calculated for a compound of two molecules of acid with one of edestin (molecular weight assumed to be 14,300), and also the correspondingly slightly greater acidity of the dissolved substance.

Edestin Sulphates.—Determinations of the solubility in sulphuric acid of edestin give tolerably uniform results for one and the same preparation, but differ for different preparations. With increasing quantities of sulphuric acid the degree of acidity of the soluble products increases uniformly up to many times that of the bihydrochlorate. This behavior with sulphuric acid is due to the fact that the preparations tested were largely hydrochlorates. Definite results cannot be had until preparations free from acids other than sulphuric have been made and tested, which work we now have in hand.

What has been said of sulphuric acid applies, though to a less degree, to phosphoric acid, a centinormal solution of which dissolves about one third as much edestin as a like solution of hydrochloric acid. In other words, tribasic phosphoric acid in dissolving edestin appears to act as a monobasic acid.

A study of the relations to bases and acids exhibited by many other protein substances is in progress, the results of which will be published soon. So far as yet discovered, all other protein preparations are compounds of a similar character to those of edestin. Although much evidence to this effect has been obtained, details are reserved until the entire accuracy of the results is confirmed and the study extended so that it may be made more complete.

It is unnecessary to point out the importance of the fact that what have been heretofore regarded as "native" protein substances are, in fact, protein bodies combined to acids, so that preparations as usually obtained have been mixtures of the simpler salts of these bodies. In this fact we will doubtless find an explanation of many of the minor differences noted between protein preparations which appear to be otherwise identical. Thus, the difference between the albumins of the eggs of different kinds of birds, between the haemoglobins of the blood and the caseins of the milk of different animals may well be thus explained.

Courrant's studies of the proportion of alkali and acid neutralized by casein makes it seem highly probable that nucleoalbumins will prove to be phosphoric acid compounds similar to those described in this paper, but containing several molecules of acid.

Fuerth's account of the protein bodies of the muscle plasma indicates that the confusion which has existed in relation to these substances is probably due to the formation during extraction and separation of a series of increasingly acid compounds of one or more protein bodies. The sensitiveness of many enzymes to alterations in reaction is not improbably connected with the formation of definite acid compounds.

The unexplained, apparently spontaneous, alteration of protein substances is in many cases certainly due to the formation of acid compounds.

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[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, NO. 7.]

THE THEORY OF THE FORMATION OF NICKEL SULPHIDE.

BY J. LIVINGSTON R. MORGAN AND A. H. GOTTHELF.

Received March 7, 1898.

NICKEL sulphide is precipitated from alkaline solutions by hydrogen sulphide gas, and when once formed is insoluble in dilute acids. Notwithstanding this insolubility, however, the precipitate is not formed when the gas is passed through a solution containing this strength of acid. By following out the general laws as to the formation of the metallic sulphides it is possible to explain this anomalous behavior in quite a simple way, and the object of this paper is to present and prove this theory as applied to nickel sulphide. Since cobalt sulphide behaves in the same manner, it is not necessary to go into details regarding it. As yet it is not known whether ions of sulphur exist in the free state, $\overset{--}{S}$, or are always combined with hydrogen in the form $\overset{-}{HS}$. *In this paper we shall consider that free ions of sulphur, $\overset{--}{S}$, do exist, but it is only for the sake of simplicity.* If hydrogen sulphide ionizes according to the scheme,

$$H_2S = \overset{+}{H} + \overset{-}{HS},$$

then all sulphides will do the same; *viz.*,

$$MS + H_2O = \overset{+}{M} + \overset{-}{HS} + \overset{-}{OH},$$

so that the relation of the concentrations of $\overset{-}{HS}$ ions in the two sulphides will be the same as would that of the $\overset{--}{S}$ ions, if they were formed. Since the sulphide is formed, it is simpler to consider $\overset{--}{S}$ ions to be present, for then the sulphide is formed directly. When $\overset{-}{HS}$ ions are present the reaction would be

$$\overset{++}{M} + 2\overset{-}{Cl} + 2\overset{-}{HS} + 2\overset{+}{H} = MS + H_2S + 2\overset{+}{H} + 2\overset{-}{Cl},$$

the result being the same, but reached in a more complicated way. It is to be remembered then that, although we speak of $\overset{--}{\mathrm{S}}$ ions, it is not necessary that they exist, for all conclusions will still hold with $\overset{-}{\mathrm{HS}}$ ions, providing only that the metallic sulphides dissociate in the same way as hydrogen sulphide does, a fact which is well known.

All substances are soluble to a certain extent, the term insoluble being only a relative one. Nickel sulphide in water, then, goes into solution to a certain extent, as undissociated nickel sulphide and as ions of $\overset{++}{\mathrm{Ni}}$ and $\overset{--}{\mathrm{S}}$. The equation of equilibrium which regulates the amount of each of these products is

$$\overset{++}{\mathrm{Ni}} \times \overset{--}{\mathrm{S}} = \mathrm{K}_0 \times \mathrm{NiS}\ ;$$

i. e., the product of the concentrations of the ions is equal to the concentration of the undissociated portion multiplied by the ionization constant, the concentrations being expressed in gram-molecules per liter. According to Nernst in a saturated solution, the undissociated portion always remains constant. If by any means, then, the dissociation is driven back, a certain amount of undissociated nickel sulphide will be formed, which will separate out as a solid, since the solution is already saturated with it. In the equation of equilibrium we have, then, two constant terms upon the right side, hence the left side must also remain constant ; *i. e.*,

$$\overset{++}{\mathrm{Ni}} \times \overset{--}{\mathrm{S}} = K.$$

This term K is called the *solubility product* of the nickel sulphide. The meaning of K in words is as follows: If $\overset{++}{\mathrm{Ni}}$ and $\overset{--}{\mathrm{S}}$ ions are present together in a liquid, no undissociated nickel sulphide will be formed until this product is exceeded, in which case enough undissociated nickel sulphide will be formed to cause the product of the concentrations of the ions still free to just reach this value, K. The undissociated NiS will first saturate the solution, the remainder separating out as a solid. The amount of $\overset{++}{\mathrm{Ni}}$ ions will be the smaller the greater the amount of $\overset{--}{\mathrm{S}}$ ions, for the product must remain constant. If in a solution we have a small number of metal ions, it is necessary to have an excess of $\overset{--}{S}$ ions in order that the solubility product may be exceeded, and undissociated sulphide formed. The smaller the solubility product the smaller will be the number of $\overset{--}{S}$ ions necessary for precipitation. Upon the size of the solubility product depends, then, the behavior of the salt solutions of a metal toward hydrogen sulphide gas. If the product is small enough to be exceeded by the aid of the ions of $\overset{-}{S}$ contained in a solution of hydrogen sulphide gas, the metal will belong to one of the higher analytical groups. If the product is large, then it will only be reached by an alkaline sulphide, for that contains more ions of $\overset{--}{S}$ than a saturated solution of hydrogen sulphide gas. We can divide the metals, then, into two groups, those which have products which can be exceeded by the $\overset{--}{S}$ ions in hydrogen sulphide solution, and those whose products can only be exceeded by a greater number of $\overset{--}{S}$ ions. Metals of the former class will be precipitated by hydrogen sulphide in neutral or acid solutions, those of the latter only in alkaline solutions. Some metals are partly precipitated in neutral solutions. This is due to the fact that the solubility product is at first exceeded by the simple hydrogen sulphide solution. Later, since acid is formed by the reaction, the $\overset{+}{H}$ ions increase and cause the $\overset{--}{S}$ ions of the hydrogen sulphide to decrease to such an extent that the product is no longer exceeded. The amount of the sulphide precipitated from the neutral salt depends, then, upon the strength of the acid formed, for the greater its dissociation constant the more the dissociation of the hydrogen sulphide will be affected. Since nickel, cobalt, and zinc are precipitated by hydrogen sulphide in presence of weak acids, their sulphides partake of the characteristics of the higher as well as of the lower group of metals. The solubility products must therefore be smaller than those of the others of the iron group and greater than those of the copper group. We see, then, that the division between the two general groups is not sharply defined, and so we should expect to find an anomalous action of some kind in connection with the metals of the middle group. In the case with zinc this is not observed because it partakes more of the characteristics of the upper than the lower group, but with nickel and cobalt it is marked. When nickel sulphide is brought in contact with strong hydrochloric acid, hydrogen sulphide gas and nickel chloride are formed. Hydrogen sulphide, however, can only be formed when the product of the concentration of $\overset{+}{H}$ ions multiplied by that of the $\overset{-\,-}{S}$ $(\overset{-}{HS})$ ions exceeds the solubility product. Then the gas formed saturates the solution and is given off in the gaseous state. A sulphide which in a water solution has a larger concentration of $\overset{-\,-}{S}$ ions than exists in a saturated solution of pure hydrogen sulphide, must be soluble in acid, for the product $\overset{+}{H} \times \overset{-\,-}{S}$ $(\overset{-}{HS})$ will be greater than the solubility product of hydrogen sulphide. Such a sulphide could also only be formed in an alkaline solution; *i. e.*, one in which there is a greater number of $\overset{-\,-}{S}$ ions than in hydrogen sulphide. The process of solution is quite simple, ions of $\overset{+}{H}$ and $\overset{-\,-}{S}$ $(\overset{-}{HS})$ are together in large numbers and so unite to form undissociated hydrogen sulphide. This leaves the solution unsaturated with the ions, hence more of the sulphide dissolves and dissociates, the process continuing until all the sulphide is dissolved or all the acid used up.

A sulphide which contains a smaller number of $\overset{-\,-}{S}$ $(\overset{-}{HS})$ ions in a saturated solution than exists in a solution of hydrogen sulphide, will be insoluble in acid, since the solubility product of hydrogen sulphide cannot be exceeded, and the salts will be precipitated by hydrogen sulphide even in the presence of acid. The smaller the solubility-product of the sulphide the more rapidly will the sulphide be formed by hydrogen sulphide. The greater the solubility-product of a sulphide the more rapidly it will dissolve in acid. Nickel sulphide has a solubility-product which lies between these two extremes, and must contain in a saturated solution a slightly smaller concentration of $\overset{-\,-}{S}$ $(\overset{-}{HS})$ ions than hydrogen sulphide (otherwise nickel sulphide would not be formed in presence of acid). The difference in concentration of $\overset{-\,-}{S}$ ions must be small, for a little acid prevents the precipitation by decreasing the difference. The anomalous behavior of the sulphide is due to this small difference. To cause the sulphide to dissolve it is necessary to have $\overset{+}{H}$ ions present to such an extent that the $\overset{--}{S}$ $(\overset{-}{HS})$ ions in the hydrogen sulphide formed may be smaller in number than those of the sulphide. If the acid is of such a strength that hydrogen sulphide in it would have the same, or nearly the same, concentration of $\overset{--}{S}$ ions as the sulphide, the speed of solution will be almost infinitely slow; *i. e.*, practically no solution will take place during any short period of time. The sulphide will then remain in its original state. As the amount of acid is increased, its $\overset{+}{H}$ ions decrease the number of $\overset{--}{S}$ $(\overset{-}{HS})$ ions which are necessary to exceed the solubility-product of the hydrogen sulphide gas, and finally it is formed. The velocity of the change will increase slowly with the concentration of acid, but no sharp distinction can be made.

If we attempt to precipitate nickel sulphide from a nickel salt in the presence of acid of such strength that hydrogen sulphide has nearly the same concentration of $\overset{--}{S}$ ions as the nickel sulphide would have if it were formed, no sulphide will be formed for the velocity of formation will be almost infinitely slow.

In short, if two substances have the same concentration of one kind of ion, the one will not be transformed into the other. If there is but a slight difference between the concentrations, the reaction will take place, but so slowly that it will not be observed until the concentration difference is marked. The substance which is present will always remain unaltered until the difference becomes great enough to cause a certain speed of reaction. This is the proposed theory for the explanation of the behavior of nickel and cobalt sulphides. In a few words it may be summed up as follows:

The concentration of $\overset{--}{S}$ $(\overset{-}{HS})$ ions in a saturated solution of nickel sulphide or cobalt sulphide is so little less than that in a saturated solution of hydrogen sulphide gas, that addition of a small amount of acid causes the latter to decrease to nearly the value of the former, so that the substance which is already present (hydrogen sulphide or nickel sulphide) remains unchanged, owing to the slight velocity of the change which is proportional to the difference in concentration of the two with respect to the $\overset{-\,-}{S}$ ($\overset{-}{HS}$) ions.[1]

As to the proof for this, the fact that the sulphide is formed in the presence of a large amount of acetic acid and also in that of a small amount of hydrochloric acid shows that the formation is simply a question of the concentration of sulphur ions. Neutral solutions, as the dichloracetate, allow a certain amount of precipitate to be formed; *i. e.*, until the concentration of the $\overset{+}{H}$ ions of the acid formed causes the two concentrations of $\overset{-\,-}{S}$ ($\overset{-}{HS}$) ions to become equalized. The clearest proof would be to compare the solubility-products of the nickel sulphide and hydrogen sulphide,[2] but, unfortunately, this is impossible, for neither is known. It seems, however, hardly necessary to go to such an extent as this to prove the correctness of the theory, for it is thought that the results which have been given already and those that follow are conclusive, although such a final comparison would be of interest.

The results of the analyses given below show quantitatively just what effect an acid has upon the amount of nickel sulphide formed. The amount precipitated in nickel dichloracetate is too small, for the latter was found afterward to contain free acid, the amount of which could not be determined. Nickel acetate is almost completely precipitated in a neutral solution, which was partly prevented by the addition of varying amounts of hydrochloric acid, and the amount of nickel sulphide determined.

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[1] Since writing the above, mention of an experiment has been found which is perhaps the best proof of the theory advanced. Baubigny (*Compt. rend.*, 94, 961, 1183, 1251, 1417, 1473, 1595, 1715: 95, 34) found that neutral solutions of the salts of nickel are completely precipitated by hydrogen sulphide in one month's time. This shows that the formation of the sulphide takes time and that its non-formation is due to the fact that the process is too slow to be observed during an ordinary analytical precipitation. In the same way it is probable that acid would dissolve the sulphide in the course of time, even when it has no effect as ordinarily attempted.

[2] A method for the determination of S ions in general is the subject of an investigation in the laboratory now, and if results are obtained this comparison will be made.

	Mols. per liter.
Nickel dichloracetate, concentration	0.253
Dichloracetic acid	0.1424
Nickel salt precipitated as nickel sulphide	0.00722
Dichloracetic acid formed	0.0144
Nickel salt remaining in solution	0.24

	Mols. per liter.
Nickel acetate, concentration	0.071
Hydrochloric acid	0.78
Nickel salt as nickel sulphide	0.019
Nickel salt left in solution	0.052

The acetic acid formed in these cases was neglected on account of its slight dissociation.

	Mols. per liter.
Nickel acetate, concentration	0.0624
Hydrochloric acid	0.083
Nickel salt as nickel sulphide	0.003
Nickel salt left in solution	0.0594

	Mols. per liter.
Nickel acetate, concentration	0.0788
Hydrochloric acid	0.0807
Nickel salt as nickel sulphide	0.0139
Nickel salt left in solution	0.0649

	Mols. per liter.
Nickel acetate, concentration	0.0723
Hydrochloric acid	0.079
Nickel salt as nickel sulphide	0.0112
Nickel salt left in solution	0.0601

Although the solubility products of the metallic sulphides are unknown there is one way in which we may get an approximate relation between them. Zengelis[1] has determined the electromotive force of several kinds of metal ions in contact with tenth-normal solutions of potassium sulphide. Neumann[2] has determined the electromotive force of all the metals in their salt solutions. By combining these measurements by the method of Ostwald[3] it is possible to find the ionic concentrations of the metals in contact with the same, but an unknown amount of $\overset{--}{S}$ $(\overset{-}{HS})$ ions. For each metal we have a certain solubility-product; *i. e.*,

$$M \times S = K,$$

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[1] *Ztschr. phys. Chem.*, 12, 311.

[2] *Ibid.*, 14, 215.

[3] Lehrbuch d. allg. chem., II_1, 881.

where *S* and *K* are unknown. *S*, however, is the same in the case of all metals; *i. e.*, the concentration of $\overset{--}{\mathrm{S}}$ ions in a tenth-normal solution of potassium sulphide, hence the solubility-products will be proportional to the ionic concentrations of the metals in the potassium sulphide solution. Using this method, a few relative solubility-products have been determined, and they serve to show the great difference between the metals of the iron group and those of the copper group.[1]

Nickel	0.0191	Concentration of metal ions in mols. per liter in presence of the $\overset{--}{\mathrm{S}}$ $(\overset{-}{\mathrm{HS}})$ ions contained in a tenth-normal solution of potassium sulphide.
Cobalt	0.0034	
Copper	0.00021	
Lead	0.000024	

Zinc, which is completely precipitated by hydrogen sulphide in acetic acid, should have a product still smaller than cobalt, which is not. Cobalt and zinc show the disappearance of the anomalous behavior, cobalt having it to a smaller extent than nickel, and zinc not showing it at all. We see from the results that the solubility-product of nickel sulphide is about 100 times greater than that of copper sulphide and 1000 times greater than that of lead sulphide. This means that equal amounts of solution, containing the same ionic concentration of metal ions, will be precipitated when the concentration of $\overset{--}{\mathrm{S}}$ $(\overset{-}{\mathrm{HS}})$ ions for nickel, copper, and lead are in the ratio

1000 : 100 : 1.

There is still one point to be considered in the behavior of nickel and cobalt sulphides. When the sulphides of nickel, cobalt, and zinc are treated with dilute hydrochloric acid, the zinc dissolves, leaving the sulphides of cobalt and nickel behind, notwithstanding the fact that in water zinc sulphide is more insoluble than these. This is also quite easily explained and depends simply upon the salt solution which is formed. When a sulphide is dissolved in acid, as has already been mentioned, the ions of $\overset{+}{\mathrm{H}}$ and $\overset{--}{\mathrm{S}}$ $(\overset{-}{\mathrm{HS}})$ unite to form hydrogen sulphide. This

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[1] Other determinations of the relative solubility-products are being made, and it is proposed to find also the absolute values by comparison with the value of one of the more soluble salts, determined by the method of the electrical conductivity.

removes the $\overset{--}{\mathrm{S}}$ ($\overset{-}{\mathrm{HS}}$) ions of the sulphide from the solution so that more salt dissolves and has its ions removed in the same way. Finally, we have a salt of the metal and hydrogen sulphide gas. The salt formed, if largely ionized, will prevent the sulphide from giving off enough $\overset{--}{\mathrm{S}}$ ($\overset{-}{\mathrm{HS}}$) ions to reach with the $\overset{+}{\mathrm{H}}$ of the acid, the solubility-product of hydrogen sulphide; while if but slightly ionized this effect will not be noticed. The whole process is similar to that of the formation of sulphide from a neutral salt, when the acid formed prevents the hydrogen sulphide from dissociating to an extent sufficient to cause the solubility-product of the sulphide to be exceeded. This is the process which takes place when we attempt to dissolve the sulphides of nickel, cobalt, and zinc in dilute hydrochloric acid. The chlorides of nickel and cobalt are nearly completely ionized; *i. e.*, the conductivity is found to be almost constant for all dilutions. If then a small amount of the chloride of nickel or cobalt is formed it will prevent any more being produced. In the case of zinc sulphide, however, the ionization is not so great, and, in addition, the solution is hydrolytically dissociated to a great extent. Since hydrolytic dissociation removes zinc ions from the solution, less of the depressing effect upon the solubility of the zinc sulphide is observed and it dissolves. In this way nickel and cobalt sulphides do not dissolve in acid in which zinc sulphide is soluble, since the solubility of these is depressed by the small portion which may dissolve; zinc sulphide, on the contrary, retaining its original solubility, dissolves. As a direct consequence of this the nickel and cobalt sulphides should be formed from the chlorides more readily than zinc sulphide. There are undoubtedly a number of examples of this process where the relation of solubility is reversed, but it is believed that this is the first one in the case of a salt to be observed. If it were possible to find a salt of nickel and cobalt which is ionized to a lesser degree than the corresponding one of zinc, then, if the latter were not hydrolytically dissociated, the relation in regard to solubility would be the same in the acid, which would form that salt, as in water.

ON THE DETERMINATION OF ADDED WATER IN MILK.

By A. G. Woodman.

Received March 4, 1899.

In order to estimate the amount of water which has been added to a sample of milk, it is generally necessary to make separate determinations of the specific gravity, the total solids, and the fat. The accurate determination of at least two of these factors is a matter of considerable time, and, although it is possible to shorten the time to a certain extent by the use of such formulas as those of Fleischmann, or of Hehner and Richmond, there can be no doubt that a rapid, and at the same time accurate, method for determining the extent to which milk has been watered would find extensive application.

The most successful of the various methods by which it has been proposed to effect this direct determination of added water are based, in general, upon the fact that under certain conditions the serum or liquid portion of sour milk possesses a fairly constant composition, much more so than the milk itself. The methods by which the milk serum is obtained depend for the most part upon the coagulation of the milk by means of dilute acid. Vieth[1] recommends letting the milk sour spontaneously by standing at the room temperature for two or three days and then separating the serum from the coagulum at 65° C. Other investigators prefer to coagulate the milk directly by the addition of an acid. Dietsch[2] and Radulescu[3] use dilute acetic acid and warm the milk. Reich[4] recommends the use of a small quantity of glacial acetic acid and final heating of the milk to 100° C. Sambuc[5] heats the milk to 40°–50° with two cc. of an alcoholic solution of tartaric acid of a specific gravity of 1.030–1.032, approximately the same as that of the milk serum itself. The whole question has been investigated quite thoroughly by Radulescu, who has made a study of the conditions necessary in regard to the strength of acetic acid employed, the temperature

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[1] Forschungen auf dem Gebiete der Viehhaltung und ihrer Erzeugnisse, *1884*, (15), 334.

[2] *Chem. Ztg.* (*1884*), 323.

[3] Mitt. aus dem pharm. Ins. und Laboratorium für ang. Chem. der Univ. Erlangen, (*1890*), III, 93.

[4] *Milch Ztg.*, (*1892*), 274.

[5] Jour. de Pharm. et de Chim., (*1884*), 95.

to which the mixture should be heated, and the time required, in order to obtain satisfactory results. The method recommended by Radulescu is as follows: To 100 cc. of the milk is added two cc. of twenty per cent. acetic acid, and the mixture is heated in a water-bath at 85° C. for five or six minutes, as a result of which the casein separates in the form of a compact cake and is easily filtered off. After being thoroughly mixed the filtrate is cooled to 15° C. and its specific gravity taken. The acid used is variously stated in different portions of Radulescu's paper to be "twenty per cent. acetic acid," "twenty-five per cent. acid," and acetic acid having a specific gravity of 1.0294, which is about twenty-two per cent. strength. In the determinations which I have carried out, using practically the same method as that proposed by Radulescu, I have found that for the richer samples of milk the twenty per cent. acid is too dilute, failing to entirely precipitate the casein, but that the acid of twenty-five per cent. strength is sufficient in all cases.

After a number of experiments, following at first as nearly as possible the procedure recommended by Radulescu, subsequently making such modifications in the method as were found advisable in order to secure more nearly uniform results, I have adopted the following procedure: 100 cc. of the milk, which should be at a temperature of about 20° C., are thoroughly mixed with two cc. of a twenty-five per cent. solution of acetic acid, specific gravity 1.0350, in a small beaker. The beakers, kept covered with watch-glasses, are heated for twenty minutes in a water-bath kept at a temperature of 70° C., the temperature of the milk samples being brought gradually by this means to about 65° C. The beakers are then removed from the water-bath and placed immediately in ice-water, where they are allowed to remain for ten or fifteen minutes, after which the solutions are filtered through small, dry, plaited filters, the first portion of the filtrate, which generally comes through cloudy, being returned to the filter. After the filtrate has been thoroughly mixed it is cooled to 15° C. and its specific gravity taken by means of a Westphal balance. It occasionally happens, more especially with normal milk or milk to which only a slight amount of water has been added, that the serum which is thus obtained has a slight cloudiness or opalescence, but I have not observed that it causes any appreciable difference in the specific gravity. For assistance in studying the conditions upon which the above procedure is based, I am indebted to Mr. J. W. Brown and Miss J. H. Bartlett.

In the following table (Table I) will be found the results obtained on samples of pure milk obtained from various sources, and on mixtures of these milks containing varying percentages of water, by the method that I have outlined above. All determinations of specific gravity have been made at 15° C., using a delicate Westphal balance, which gave the specific gravity of pure water at 15° C. as 1.0000.

TABLE I.

Specific Gravity.

		Serum.					
No.	Milk.	Normal.	Ten per cent. water.	Twenty per cent. water.	Thirty per cent. water.	Forty per cent. water.	Fifty per cent. water.
1.....	1.0337	1.0297	1.0263	1.0237	1.0206	1.0180	1.0153
2.....	1.0334	1.0294	1.0260	1.0232	1.0203	1.0174	1.0151
3.....	1.0340	1.0295	1.0264	1.0232	1.0206	1.0175	1.0151
4.....	1.0324	1.0293	1.0259	1.0233	1.0202	1.0178	1.0148
5.....	1.0336	1.0296	1.0262	1.0235	1.0205	1.0177	1.0153
6.....	1.0328	1.0293	1.0258	1.0233	1.0202	1.0174	1.0148
7.....	1.0334	1.0292	1.0260	1.0233	1.0202	1.0175	1.0149
8.....	1.0325	1.0294	1.0260	1.0234	1.0201	1.0175	1.0152
9.....	1.0339	1.0296	1.0262	1.0236	1.0206	1.0178	1.0153
10.....	1.0335	1.0296	1.0261	1.0235	1.0204	1.0174	1.0148
11.....	1.0329	1.0292	1.0259	1.0234	1.0203	1.0173	1.0148
Av....	1.0335	1.0294	1.0261	1.0234	1.0204	1.0175	1.0150

The specific gravity of the serum from milk at a given dilution is shown by the table to be a fairly constant quantity, the average decrease for each ten per cent. of water being 0.0031.

The specific gravities given in Table I were obtained on samples in which the per cent. of water *in the mixture* varied by ten. As might naturally be expected, if the results are calculated on the basis of percentage of *added* water the differences in specific gravity are not so great. In Table II are given the results obtained on samples of pure milk to which varying percentages of water have been added.

TABLE II.

Samples varying by ten per cent. *added* water.

		Specific Gravity.					
		Serum.					
No.	Milk.	Normal.	Ten per cent. water.	Twenty per cent. water.	Thirty per cent. water.	Forty per cent. water.	Fifty per cent. water.
1....	1.0336	1.0294	1.0259	1.0239	1.0219	1.0199	1.0189
2....	1.0333	1.0295	1.0260	1.0240	1.0220	1.0200	1.0190
3....	1.0334	1.0294	1.0259	1.0239	1.0220	1.0200	1.0190
4....	1.0330	1.0295	1.0260	1.0239	1.0221	1.0201	1.0190
5....	1.0324	1.0294	1.0259	1.0239	1.0220	1.0199	1.0190
6....	1.0328	1.0294	1.0260	1.0239	1.0220	1.0200	1.0190
7....	1.0340	1.0294	1.0260	1.0239	1.0220	1.0200	1.0190
8....	1.0337	1.0296	1.0261	1.0240	1.0221	1.0201	1.0190
9....	1.0330	1.0294	1.0259	1.0239	1.0221	1.0200	1.0190
10....	1.0335	1.0295	1.0260	1.0239	1.0220	1.0199	1.0189
Av...	1.03327	1.02945	1.02597	1.02392	1.02202	1.01999	1.01898

These results confirm the conclusion reached by Radulescu, that the specific gravity of the serum from normal milk is never below 1.027, and in no case of those examined was it found to be below 1.0290. The decrease in specific gravity caused by the addition of ten per cent. of water varied from 0.0035 to 0.0010. The statement is made by Radulescu,[1] that the addition of each ten per cent. of water to normal milk lowers the specific gravity of the serum by 0.0005 to 0.0010 and this value is also given by König.[2] This is evidently an error, for from the preceding table it will be seen that the decrease actually obtained is considerably higher and as a matter of fact the differences shown in Radulescu's tabulation of results vary from 0.0029 to 0.0012. I do not consider it advisable to determine the amount of total solids and of fat in the milk serum, as recommended by Radulescu, because if this is done the method offers no special advantages as far as regards economy of time and ease of execution over those ordinarily used.

The method as originally proposed by Radulescu has been criticised by E. Reich[3] on the ground that only a partial clarification of the milk is effected, the precipitation and removal of the albumen not being complete at the temperature to which the

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[1] *Loc. cit.*

[2] Die Untersuchung landwirtschaftlich und gewerblich wichtiger Stoffe, Ed. (*1898*), 361.

[3] *Milch Ztg.*, (*1892*), 274.

mixture is heated. The following modification of the method has been proposed by Reich : 100 cc. of the milk is thoroughly shaken in a 200 cc. flask with four-tenths cc. glacial acetic acid, the mixture heated for five or six minutes at 60°–65°, cooled, and the liquid portion poured off into fifty cc. Erlenmeyer flasks. These are hung for five or six minutes in a boiling water-bath, then rapidly cooled in ice-water. The casein and albumen are removed by filtering through a small dry Swedish filter and the specific gravity of the filtrate taken at 15° C. I have determined the specific gravity of the serum from five samples of milk diluted with varying percentages of water by Reich's method and also of the same samples by the modification of Radulescu's method previously described. These results are given in the following Table (III):

TABLE III.

Specific gravity.

		Serum.					
No.	Milk.	Normal.	Ten per cent. water.	Twenty per cent. water.	Thirty per cent. water.	Forty per cent. water.	Fifty per cent. water.
		According to Radulescu's Method Modified.					
1......	1.0337	1.0294	1.0259	1.0239	1.0220	1.0199	1.0100
2......	1.0319	1.0294	1.0260	1.0240	1.0220	1.0199	1.0190
3......	1.0338	1.0295	1.0260	1.0239	1.0220	1.0200	1.0189
4......	1.0340	1.0294	1.0259	1.0239	1.0219	1.0200	1.0189
5......	1.0328	1.0294	1.0260	1.0240	1.0220	1.0200	1.0190
		Same Samples According to Reich's Method.					
1......	1.0337	1.0293	1.0266	1.0240	1.0224	1.0205	1.0196
2......	1.0319	1.0289	1.0257	1.0234	1.0219	1.0200	1.0182
3......	1.0338	1.0292	1.0264	1.0245	1.0226	1.0207	1.0199
4......	1.0340	1.0296	1.0264	1.0243	1.0225	1.0205	1.0198
5......	1.0328	1.0295	1.0270	1.0247	1.0217	1.0210	1.0199

The claim of Reich that his method yields concordant results which are uniformly lower than those obtained by Radulescu's method is not borne out by the figures shown in the above table. It has been my experience that the method offers no advantages over that of Radulescu, being more tedious to carry out and giving results which vary more widely.

As an illustration of the degree of accuracy with which the amount of added water in milk may be estimated from the specific gravity of the milk serum I give the following results obtained on two samples purchased at a city grocery and supposed to be pure milk:

	1.	2.
Specific gravity milk	1.0282	1.0263
" " serum	1.0257	1.0234

The specific gravity of the serum indicated in one case ten per cent. and in the other twenty per cent. of added water. The amount of added water calculated from careful determinations of the total solids and of the fat was very close to this, being 9.8 per cent. for the first sample and 19.6 per cent. for the second. The method is easy to carry out and should prove to be of considerable value.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
February, 1899.

[CONTRIBUTION FROM THE DIVISION OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE, NO. 33.]

DETERMINATION OF CALCIUM AND MAGNESIUM IN ASHES.[1]

BY J. K. HAYWOOD.

Received March 15, 1899.

THOSE who have had any considerable number of ash samples to analyze according to the method adopted by the Association of Official Agricultural Chemists, cannot help having been struck with the extreme difficulty of determining calcium and magnesium. The whole trouble consists in washing the voluminous precipitate of basic acetate of iron and phosphate of iron, which is not only so bulky as to be troublesome, but also commences to run through the filter soon after washing is begun.

The following work was undertaken with the idea of showing that this washing can be entirely done away with, without seriously affecting the accuracy of the results. To do this the precipitation of the phosphoric acid and iron from the solution of calcium and magnesium was made in a 500 cc. flask, the solution then cooled to room temperature, made up to the 500 cc. mark, and *well shaken*. 250 cc. of this solution were then filtered off through a dry filter, keeping the funnel covered to prevent evaporation, evaporated to a small volume, ammonia added to get rid of any small traces of iron that might have dissolved in

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[1] Read at the meeting of the Washington Section, March, 1899.

the liquor (nothing like the large amount that comes through the filter when the precipitate is washed), and the solution again filtered. • The manganese is removed with bromine and ammonia, and calcium and magnesium determined in the filtrate. It will be noticed that this method does not correct for the volume occupied by the precipitate of basic acetate of iron and phosphate of iron, and it was to show that this correction is immaterial that the following work was undertaken.

For purposes of analysis three powders were prepared: one containing approximately ten per cent. of lime, three and five-tenths per cent. of magnesia, and 86.5 per cent. of sand; two containing twenty per cent. lime, five per cent. of magnesia, and seventy-five per cent of sand; and three containing thirty per cent. of lime, nine per cent. of magnesia, and sixty-one per cent. of sand. Ten grams of each powder were dissolved in hydrochloric acid and filtered to a volume of 500 cc., aliquot portions being taken for analysis.

Analyses of the above powders showed the following per cents. of calcium and magnesium oxides:

	I.	II.	III.
Lime	9.81	19.74	29.78
	9.85	19.66	29.86
Average	9.83	19.70	29.82
Magnesia	3.69	5.28	8.90
	3.71	5.26	8.90
Average	3.70	5.27	8.90

Aliquot portions were again taken from the solutions prepared as above and phosphoric acid was added to each portion, amounting in the case of solution I to five per cent. of the total amount of powder used, in the case of solution II to ten per cent. of the total amount of powder used, and in the case of solution III to twelve per cent. of the total amount of powder used. Enough ferric chloride was added to precipitate all phosphoric acid, and these portions analyzed according to my method mentioned above, with the following results:

	I.	II.	III.
Lime	9.80	19.72	29.52
	9.76	19.80	29.54
Average	9.78	19.76	29.53

	I.	II.	III.
Magnesia	3.75	5.21	8.95
	3.82	Lost	8.93
Average	3.79	5.21	8.94

showing practically the same results as those obtained above when no volume of a precipitate was neglected.

In the case of solution III a rather extreme case was next tried by adding enough phosphoric acid to correspond to twenty per cent. of the original powder. The results were :

III.

Lime	29.74	Magnesia	9.19
	29.90		9.21
Average	29.82		9.20

In my work last year on the official ash sample, which contained 9.83 per cent. of phosphoric acid, the calcium and magnesium were determined according to the above method with the following results, in triplicate :

Lime	11.94	Magnesia	5.83
	11.94		5.75
	11.97		5.77
Average	11.95		5.78

as against an average of lime 11.62, magnesia 5.74, by the other chemist engaged in the work.

The results obtained arranged in tabular form were :

No. 1.

	Lime.	Magnesia.
Before adding phosphorus pentoxide	9.83	3.70
After adding five per cent. phosphorus pentoxide	9.78	3.79

No. 2.

	Lime.	Magnesia.
Before adding phosphorus pentoxide	19.70	5.27
After adding ten per cent. phosphorus pentoxide	19.76	5.21

No. 3.

	Lime.	Magnesia.
Before adding phosphorus pentoxide	29.82	8.90
After adding twelve per cent. phosphorus pentoxide	29.53	8.94
After adding twenty per cent. phosphorus pentoxide	29.82	9.20

OFFICIAL ASH.

	Lime.	Magnesia.
Washing precipitate	11.62	5.74
Not washing precipitate	11.95	5.78

In the case of ashes which contain a larger per cent. of phosphoric acid than that included in the limits of this paper, a small correction may be necessary for the volume occupied by the precipitate. On account of lack of time I will reserve the investigation of this subject for a future paper.

THE EFFECT OF DI-IONIC ELECTROLYTES ON THE SOLUBILITY OF TRI-IONIC ELECTROLYTES WITH DIFFERENT IONS.[1]

BY ARTHUR A. NOYES AND EDWARD S. CHAPIN.

Received March 3, 1899.

1. THE OBJECT OF THE INVESTIGATION.

THE theory of the effect of one di-ionic electrolyte upon the solubility of another with different ions has already been developed by Noyes[2], and confirmed by our researches[3] and those of Noyes and Schwartz.[4] The solubility of tri-ionic electrolytes in the presence of other electrolytes with an ion in common has also been investigated.[5] The solubility of tri-ionic electrolytes in the presence of other electrolytes with different ions has, however, heretofore not been considered, except from a purely theoretical standpoint. The object of this article is to discuss theoretically a special case of this phase of solubility effect, and to communicate experiments, which confirm the theory. The special case chosen is the solubility of calcium hydroxide in the presence of ammonium chloride, in which case a weakly dissociated substance, ammonium hydroxide, is formed by metathesis.

2. THEORY OF THE SOLUBILITY EFFECT.

Consider a solution of any di-ionic electrolyte, CD, which is saturated with a tri-ionic electrolyte, AB_2. In accordance with the reaction

$$AB_2 + 2CD = AD_2 + 2CB$$

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[1] Read at the Boston Meeting of the American Chemical Society, August 25, 1898.

[2] *Ztschr. phys. Chem.*, 27, 267.

[3] This JOURNAL, 20, 751.

[4] *Ibid.*, 20, 742.

[5] *Ztschr. phys. Chem.*, 9, 623; 26, 152.

certain quantities of the undissociated substances AD_2 and CB will be formed, so that the solubility of AB_2 will be greater than that in pure water; for it exists in the solution not only in the form AB_2 and its ions (as in pure water), but also in the form AD_2 and CB. Suppose that the substances CD and AD_2 are strongly dissociated, in which case their undissociated amounts may be determined with sufficient exactness from their electrical conductivities;[1] and suppose that the substance CB on the contrary is only slightly dissociated, and that it conforms to the laws of mass action. Designate the molecular concentrations of the ions A, B, C, and D by the same capital letters; the molecular concentrations of the undissociated portions of the four substances AB_2, CD, AD_2, and CB by a, b, c, and d respectively; the solubility of AB_2 in pure water by m_0; the corresponding degree of its dissociation by a_0; the solubility of AB_2 in a solution of CD of concentration n by m; the product $4\,m_0^3a_0^3$ by k_a; and the dissociation constant of CB by k_d. The two following equilibrium equations then hold true, the first expressing the constancy of the product of the concentrations of the ions of any tri-ionic salt with which a solution is saturated, and the second the relation between the concentration of the undissociated portion and those of the ions of any di-ionic salt.

$$A \times B^2 = k_a \tag{1}$$

$$C \times B = k_d d \tag{2}$$

From the conditions of the case the three following equations may be derived:

$$A + a + c = m \tag{3}$$

$$B + 2a + d = 2m \tag{4}$$

$$C + b + d = n \tag{5}$$

These five equations contain only five unknown quantities A, B, C, d, and m, and can therefore be solved for m. For brevity we substitute

$$x = m - a,\ e = n - b \text{ and } r = \frac{4\,k_d^2}{k_a}.$$

After elimination the following equation is obtained:

$$rx^4 - (2\,rc + 4)x^3 + (rc^2 + 4e + 4\,c)x^2 - [(k_d + e)^2 + 4\,ec]x + [c(k_d + e)^2 + k_a] = 0, \tag{6}$$

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[1] Ztschr. phys. Chem., 27, 270.

an equation, which after the substitution of the numerical values, may be solved in the usual manner. The method of calculating the values of b and c (here considered to be known) will be explained later by an example.

When the solutions of AB_2 or of CD are very dilute, or when in the case of moderately concentrated solutions approximate values only are desired, the values of b and of c may be neglected, and the equation becomes

$$rx^4 - 4x^3 + 4nx^2 - (k_d + n)^2x + k_a = 0. \qquad (7)$$

When, on the contrary, as in the case to be considered, the substance AB_2 is moderately soluble, the concentration of CD is considerable, and the substance CB is slightly dissociated—the values r, k_d, and b are negligible, while c is appreciable. The equation then becomes

$$4x^4 - 4(n + c)x^2 + (n^2 + 4nc)x - (cn^2 + k_a) = 0. \qquad (8)$$

3. DESCRIPTION OF THE EXPERIMENTS.

In order to test these principles, we have determined the solubility of calcium hydroxide in water and in three ammonium chloride solutions of different concentrations. The calcium hydroxide was prepared from a supposedly pure sample of the same by dissolving in hydrochloric acid, treating with ammonium hydroxide to remove other metals, precipitating with ammonium carbonate, and igniting this precipitate just before using in small portions in a platinum crucible. The ammonium chloride was prepared by precipitating with strong hydrochloric acid, a concentrated solution of the commercial article, and three times recrystallizing the product from hot water. Two solutions of ammonium chloride, each about 0.087 normal, were prepared independently. From these were prepared by dilution solutions of one-half and one-fourth the original concentration. The concentrations of the strong solutions were determined gravimetrically by precipitation with silver nitrate.

The solutious were saturated in the usual manner.[1] As they would not settle, they were filtered.

On account of the tendency of the calcium hydroxide to absorb carbon dioxide from the air, this was done in air free from this gas within a vacuum desiccator containing potassium hydroxide.

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[1] *Ztschr. phys. Chem.*, 9, 603.

The apparatus was so arranged that the saturated solutions were sucked from the bottles in which saturation took place directly into the desiccator through a hole in the top onto filters which stood in graduated flasks. The flasks were filled a little over the mark. The desiccator was then opened, the liquid in the flasks was brought exactly to the mark with filter-paper and was then emptied into Erlenmeyer flasks containing not quite enough standard hydrochloric acid to neutralize the dissolved calcium hydroxide. The titration was then quickly completed with more hydrochloric acid, using methyl orange as an indicator.

4. THE EXPERIMENTAL RESULTS.

The following table contains the values of the solubility of the calcium hydroxide at 25° expressed in millimols (thousandths of a molecular weight) per liter.

Exp. No.	Conc of NH_4Cl 0.0.	Conc. of NH_4Cl 21.76 millimols.	Conc. of NH_4Cl 43.52 millimols.	Conc. of NH_4Cl 87.03 millimols.
1	20.24	28.99	39.12	59.45
2	20.21	29.09	39.31	59.96
3	20.23	29.06	39.31	59.60
4	20.26	29.13	39.22	59.67
5	20.14	29.13	39.30	59.74
Mean	20.22	29.08	39.23	59.68

In order to test the theory, it is necessary to know in addition to these solubility values, the degree of dissociation of the substances involved. In the case of ammonium chloride, calcium chloride, and ammonium hydroxide, reliable measurements of their electrical conductivities had been previously made; but in the case of calcium hydroxide in pure water, there were no data available, and therefore we have measured it ourselves. The solutions were saturated in the rotating apparatus, and their conductivities were then measured by the usual method of Kohlrausch. The value of the molecular conductivity of a 0.02022 molecular solution of calcium hydroxide was found to be 400.7[1] at 25°. This corresponds to a degree of dissociation of 0.808, if according to Kohlrausch[2] (μ_∞ (OH) = 186) and to Bredig[3] (μ_∞(Ca) = 124), 496 is assumed as the limiting value of the molecular conductivity of calcium hydroxide.

[1] Two independent solutions gave 400.5 and 400.9.

[2] Wied. *Ann.*, 50, 408. Kohlrausch gives 165 as the value for μ_∞(OH) at 18° from which, and from the temperature coefficient, follows the value 186 at 25°.

[3] *Ztschr. phys. Chem.*, 13, 235.

5. CALCULATION OF THE THEORETICAL VALUES AND COMPARISON OF THEM WITH THE EXPERIMENTAL ONES.

We have calculated the theoretical values by equation (8); for the value of r (0.000085) and that of k_d (0.000019), are extremely small, and that of b, even in the most concentrated solution (about one-tenth normal) is but $0.001 \times n$.. The small value of b, the quantity of undissociated ammonium chloride, is explained by the fact that the concentration of the ammonium ions, on account of the weakness of the ammonium hydroxide, is extremely small. The constant k_a ($= 4m_0^2a_0^2$) which appears in the equation is equal to 0.00001748; for according to our experiments $m_0 = 0.02022$, and $a_0 = 0.808$. The value of c, the undissociated quantity of calcium chloride, varies with the value of n. In order to determine the value of c in the different cases, we have made use of the conductivity measurements of MacGregory.[1] From his data at the concentrations 0.01, 0.05, and 0.1 normal we calculated first the degree of dissociation by dividing by the limiting value ($\mu_\infty(\frac{1}{2}\,CaCl_2) = 110$), and then the empirical dissociation constant k'_c by van't Hoff's[2] formula,

$$k_c' = \frac{c_i^3}{c_s^2},$$

where c_i represents the concentration of the ions and c_s that of the undissociated substance. From this constant the values of c may then be calculated conversely with sufficient exactness by the equation:

$$k_c' = \frac{A \times D^2}{c^2},$$

in which A may be put equal to x (an estimated value of x being used) and D equal to n. The values of c thus calculated are: 0.0032 for $n = 0.0217$; 0.0074 for $n = 0.0435$; and 0.0180 for $n = 0.087$. They are, therefore, appreciable quantities.

The following table contains the calculated solubilities together with those found by experiment, both expressed in millimols per liter.

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[1] *Phys. Review*, 2, 370.

[2] *Ztschr. phys. Chem.*, 18, 300.

Concentration of ammonium chloride.	Solubility of calcium hydroxide. Found.	Calculated.
0	20.22	....
21.76	29.08	28.09
43.52	39.23	38.6
87.03	59.69	58.3

The agreement is satisfactory. The theory developed regarding the effect of di-ionic electrolytes on the solubility of tri-ionic electrolytes with different ions is therefore confirmed.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
BOSTON, March, 1899.

MEASUREMENTS OF "TURBIDITY" IN WATER.

BY W. P. MASON.

Received January 18, 1899.

THE method of expressing turbidity in words is so unsatisfactory that the writer has for some time past employed the following means of securing numerical results: The change has proved of decided advantage, particularly for an examination of filtrates and storage waters. Use is made of a brass tube two and one-half inches in diameter and two feet long, closed at the ends by disks of quarter-inch plate glass held in place by screw-caps.[1] Such tubes are easily cleaned and give excellent satisfaction.

For the purpose of measuring the amount of turbidity, a standard is prepared, consisting of one gram of exceedingly fine kaolin (obtained by elutriation) suspended in one liter of distilled water. Each cubic centimeter of this preparation will contain one milligram of suspended clay.

Having nearly filled the duplicate observation-tube with distilled water, enough of the "clay standard" is added to make the turbidity equal to that of the water under examination in the other tube. Knowing the volume of water operated upon and the amount of "clay standard" used, the turbidity expressed in parts per million can readily be calculated. It should be noted that although the tube containing the "clay standard" is, of necessity, not completely full, yet by inclining

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[1] Such tubes may be obtained from Richards & Co., 30 East 18th St., New York City.

its barrel towards a horizontal position the required observation depth of two feet is easily obtained.

Any quickly subsiding material present should be classed as sediment rather than turbidity. To determine the same it would be best to decant the water above such deposit and then catch it upon a weighed filter or in a Gooch crucible.

THE TOXIC ACTION OF SODIUM FLUORIDE.[1]

BY HERBERT B. BALDWIN.

Received April 10, 1899.

THE title of this article was suggested by a recent case of accidental poisoning by means of sodium fluoride. The substance is now largely sold as an insecticide put up in tin cans resembling baking-powder boxes. In this way and on account of its now somewhat extended use in the arts there is considerable liability of accidental poisoning from it. The possibility of future accidents, and the fact that in searching for literature on the salt as a toxic agent no record was found of any severe or fatal poisoning, induced the writer to present a brief history of the case together with such other information as could be collected.

Some pan-cakes served for breakfast were partaken of by six or seven persons. Some ate very sparingly, one woman only a portion of one, while one man ate three or four of them. All who had eaten vomited within five to fifteen minutes afterward. In some cases purging occurred, in others it did not. In one case, at least, this purging and occasional vomiting continued for a day or more, with pains in the limbs complained of.

In the case of the man who ate three or four cakes, vomiting commenced early, but he soon recovered sufficiently to attend to his duties as bartender until early in the afternoon when he was obliged to retire to his room. He died early in the evening of the same day, practically without medical attendance. Further symptoms in the case could not be ascertained.

At the time this occurred it was supposed to be a case of criminal poisoning and some milk used in mixing the cakes was suspected. An analysis, by the writer, of this milk and a portion of the viscera of the deceased failed to detect any of the usual mineral poisons. But a small amount (0.007 gram) of what

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[1] Read at the meeting of the New York Section, April 7, 1899.

looked like ordinary white sand was separated and preserved.

Further investigation by the authorities resulted in finding a box of roach poison by the side of the baking-powder box and an analysis showed it to consist of sodium fluoride which contained as an impurity a small amount of sand which was microscopically identical with that recovered from the stomach of the deceased.

This served as a clue, and although the contents of the stomach had been destroyed, a little mucus scraped from a small portion of tissue that had remained in the laboratory for six weeks, contained enough of the poison to be detected with certainty.

The mucus was macerated with a little water and filtered. The filtrate was precipitated with calcium chloride and a very small precipitate (probably two or three milligrams) of calcium fluoride obtained. This, after drying, was sufficient, when mixed with a fraction of a drop of sulphuric acid, to strongly etch a piece of glass. The sodium was detected before precipitating by means of flame coloration and the spectroscope.

There was no means of knowing exactly what the fatal dose had been in this case, but judging from the relative amounts of sand in the stomach and the roach poison, it must have been at least ten grams.

The stomach was nearly empty and contained only a small amount of a gray slimy mucus that clung rather tenaciously to the mucous membrane which was somewhat inflamed.

While the above investigation was in progress an almost identical accident occurred in another city. Here fairly accurate data were obtainable regarding the dose and symptoms.

About twenty-six grams of the fluoride were used instead of baking-powder in making twenty-six wheat cakes for breakfast. One brother ate nine, a daughter six, the mother (age sixty-nine) five and another brother one. Assuming the substance to have been thoroughly mixed, the amount taken by each was, respectively, nine, six, five and one grams.

The symptoms varied considerably as follows: The man who had taken nine grams was seized with very violent cramps almost immediately afterward. These continued at frequent intervals for about thirty-six hours and were followed by severe pain for three or four days before recovery. Purging commenced quite early and vomiting in about four hours. Retching continued for two or three days.

The daughter who had taken six grams felt sick when eating the last cake and vomited in five or ten minutes. Sometime afterward she took some mustard water and vomited again. She felt weak and sick for two days. No diarrhea.

The mother took but five grams but was the most seriously affected of all. Although the nauseous feeling commenced, as with the others, within five minutes, she did not vomit for about five hours. Diarrhea, however, began in fifteen or twenty minutes and was a serious symptom for several days. She was confined to her bed for two weeks with extreme prostration and did not completely recover for four weeks.

Information regarding the heart and lungs could not be obtained in any of these cases.

Three other cases were heard of. One was a man who was made to vomit by merely tasting the substance a few times with the object of finding out whether it was borax or not. Another one (a salesman) had tasted the salt many times a day without any ill effects. The other case was a man who, while intoxicated, took in mistake for Rochelle salts about fifty grains. He was soon taken with violent vomiting and purging but recovered in a few days.

Before these last cases cited came to the knowledge of the writer and before any literature on the subject had been found, he made the experiment of taking a few gradually increased doses of sodium fluoride to ascertain its toxic action upon himself. Merely tasting small quantities produced a slight feeling of nausea with slight salivation. 0.03 gram swallowed with some bread produced no effect. Neither did 0.09 gram taken one hour later, except a little salivation. 0.25 gram, however, taken two days afterward on an empty stomach, produced nausea in two minutes. This gradually increased in severity for twenty minutes when the period of greatest intensity was reached. There was a largely increased flow of saliva and some retching but no vomiting occurred at that time although the desire was very great. The nausea gradually subsided so that luncheon could be eaten (without relish), but vomiting took place immediately on its completion which was two hours after taking the poison. Slight nausea continued throughout the following day but disappeared on the second day.

Although some of the toxic properties of sodium fluoride have long been known, no reference was found in the literature of anyone who had taken a large dose of it. This is probably due to its very limited commercial use in former days.

As long ago as 1867 Rubuteau[1] in experiments on dogs and rabbits found that in dogs five-tenths gram given by the mouth made them sick but that 0.25 gram was without action. One gram injected into the blood caused serious symptoms but was not fatal. In rabbits 0.25 gram by the mouth made them sick and the same amount injected was fatal.

These results do not agree, as regards the lethal dose, with similar experiments made later by others, and Rubuteau afterward says that the purity of the fluoride used was questionable.

Kolipinski[2] in 1886 used it medicinally with good results in sympathetic headache, intermittent fever and epilepsy in doses of less than a quarter of a grain, larger doses being liable to cause nausea. He says "that five grains given to a dog on meat produces vomiting in a few minutes which continues until the stomach is empty, and may then cease or end a little later with much retching or ejection of mucus. * * *

"The intravenous injection of a toxic dose (three grains for the cat) produces in this animal and in the dog death in a few hours." * * * With the vomiting may occur evacuation of feces and urine. * * * At intervals there are moments of unrest with twitchings or tremors of the limbs. For the most part the animal is quiet and unconscious. This stage begins with the cessation of vomiting which ends within the first hour. * * * The urine is slightly albuminous and rich in fluorine."

The same authority describes an experiment where he gave at the same time to each of three males one-eighth of a grain of sodium fluoride. The urine voided at that time soon became turbid at the room temperature, while that passed two hours later remained clear for seven days from the perservative effect of the

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[1] Étude experimentale sur les effets physiol. des fluorures. Paris, 1867.

[2] *Med. News*, 49, No. 8, Philadelphia, *1886*.

fluorine eliminated. Urine passed one to two hours afterward quickly decomposed as usual.

Shulz,[1] 1889, found that when subcutaneously injected, the lethal dose of sodium fluoride was for rabbits 0.2 to 0.4 gram, for dogs 0.3 gram and for frogs 0.005 to 0.006 gram.

Haidenhain,[2] 1889, stated that 0.05 to 0.10 gram for kilogram of body weight injected into the blood of dogs produced death.

Weinland,[3] 1894, in experimenting with the sodium salts of the halogens on mucous membrane from the throat of the frog found that equimolecular solutions killed the membrane in the following orders: Sodium fluoride (two and one-tenth per cent.) in one minute; sodium iodide (seven and five-tenths per cent.) in ten minutes; sodium bromide in forty-five minutes, and sodium chloride (two and nine-tenths per cent.) in sixty minutes.

P. Grützner,[4] 1893, found the same order of sensitiveness for nerves.

Czrellitzer,[5] 1895, after reviewing the work of others, concludes that sodium fluoride is an active poison for micro-organisms of all kinds, algae, and nerves and muscles of the higher organisms. He proves that the poisonous action is stronger on some kinds of cells than others. After citing the theories of several authors he believes there is no satisfactory explanation of the way in which it exerts its poisonous action.

It appears from the evidence thus far obtained that the most characteristic symptoms produced by sodium fluoride in the individual are early nausea, vomiting, and salivation. Its detection may be accomplished, as in the case cited, by precipitating the solution with calcium chloride and testing the calcium fluoride obtained for fluorine. The results of Kolipinski's experiments indicate that an examination of the urine would also be important in cases of suspected poisoning.

The facts ascertained seem sufficient to class sodium fluoride among the less violent poisons and as such it ought to find a place in works on toxicology.

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[1] Untersuchungen über die Wirkung des Fluornatriums und der Flüssaure: Arch. f. exp. Path. und Ther., 1889.

[2] Neue Versuche über die Aufsaugung im Dündarm.—Pflüger's Arch., 1894.

[3] Ueber Chemische Reizung des Flimmerepithels.—Pflüg. Arch., 58, 1894.

[4] Ueber Chemische Reizung Motorische Nerven: Pflüg. Arch., 53, 1893.

[5] Zur Kentniss des Fluornatrium, Inaugural Dissertation, Breslau, 1895.

[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, No. 8.]

THE THEORY OF THE SEPARATION OF BARIUM, STRONTIUM, AND CALCIUM FROM THE MIXED SULPHATES.

BY J. LIVINGSTON R. MORGAN.

Received March 28, 1899.

A mixture of a soluble sulphate and carbonate transforms strontium and calcium sulphates into carbonates, leaving barium sulphate unchanged. Ammonium carbonate has also this same effect, so that the use of the soluble sulphate seems superfluous. The object of this paper is to show the action with both solvents, to calculate the effect of the sulphate added or formed, and also to show how the theories of physical chemistry may be applied to analytical chemistry. By Nernst's Laws,[1] for saturated solutions the undissociated portion of an insoluble salt remains constant even after addition of a salt with an ion in common. In the equation of equilibrium for a binary salt,

$$Kc = c_1c_2, \qquad (1)$$

where c is the concentration of undissociated salt (in gram-molecules per liter) and c_1 and c_2 are those of the two ions, K being the ionization constant; K and c are both constant for a saturated solution, hence

$$c_1c_2 = \text{constant} = \text{solubility product}. \qquad (2)$$

The meaning of this product may be expressed as follows: for any one constant temperature the two ions may exist free to such a concentration that the product just reaches this value. If we add to such a solution a salt with an ion in common, an undissociated portion is formed from equivalent amounts of the two ions, until the product of those remaining just reaches the value of the solubility product. The undissociated portion being increased by the addition, it is necessary that a certain amount of it separates out in the solid form, since the solution was saturated. In exactly the same way a substance is always less soluble in a solution containing an ion in common than it is in pure water. In such a case, one ion being present to a large extent, the substance can dissolve only so long as the product of the concentration of the one ion into the sum of those of the two portions of the other is less than or

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[1] See Morgan and Gotthelf: This Journal, 21, 494.

equal to the solubility product. These relations are best shown by an alteration of equation 2; we have then,

$$c_1'(c_2'+x) = \text{solubility product}, \qquad (3)$$

when $c_1' = c_2'$ is the present solubility of the salt, in terms normal, and x is the concentration of the ions added, expressed in the same terms. When x and the solubility product are both known it is simple to find $c_1' = c_2'$; or when $c_1' = c_2'$ is known as well as the solubility product we can find x. In all cases where $c_1' = c_2'$ is very small and x is large, c_2' may be neglected as compared with x and we have

$$c_1'x = \text{solubility product}. \qquad (4)$$

In all cases of insoluble salts such as those used in an analysis, we may neglect the undissociated portion, and consider the major portion of the substance as present in the ionic state, for in such dilute solutions the undissociated portion, while still existing, must be exceedingly small.

By use of these equations, and especially (2) and (3), it is possible to calculate from the solubility of a substance in water its solubility product and also its solubility in presence of like ions of any definite concentration. The solubilities which form the basis of this paper are taken from Holleman.[1]

For the sulphates and carbonates of barium, strontium and calcium by (2) at 20° C., we have,

$$\overset{++}{\mathrm{Ba}} \times \overset{--}{\mathrm{SO_4}} = 0.0000000001 \qquad (5)$$

$$\overset{++}{\mathrm{Ba}} \times \overset{--}{\mathrm{CO_3}} = 0.0000000105 \qquad (6)$$

$$\overset{++}{\mathrm{Sr}} \times \overset{--}{\mathrm{SO_4}} = 0.00000029 \qquad (7)$$

$$\overset{++}{\mathrm{Sr}} \times \overset{--}{\mathrm{CO_3}} = 0.000000005 \qquad (8)$$

$$\overset{++}{\mathrm{Ca}} \times \overset{--}{\mathrm{SO_4}} = 0.0029 \qquad (9)$$

$$\overset{++}{\mathrm{Ca}} \times \overset{--}{\mathrm{CO_3}} = 0.0000000154 \qquad (10)$$

In saturated water solutions of these salts we have then ionic concentrations as follows:

$$\overset{++}{\mathrm{Ba}} = \overset{--}{\mathrm{SO_4}} = 0.00001 \text{ normal} \qquad (11)$$

$$\overset{++}{\mathrm{Ba}} = \overset{--}{\mathrm{CO_3}} = 0.0001 \quad \text{``} \qquad (12)$$

$$\overset{++}{\mathrm{Sr}} = \overset{--}{\mathrm{SO_4}} = 0.00054 \quad \text{``} \qquad (13)$$

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[1] *Ztschr. phys. Chem.*, 12, 125–139.

$$\overset{++}{\mathrm{Sr}} = \overset{--}{\mathrm{CO}_3} = 0.00007 \text{ normal} \qquad (14)$$

$$\overset{++}{\mathrm{Ca}} = \overset{--}{\mathrm{SO}_4} = 0.054 \quad \text{``} \qquad (15)$$

$$\overset{++}{\mathrm{Ca}} = \overset{--}{\mathrm{CO}_3} = 0.000124 \quad \text{``} \qquad (16)$$

We see from these results that the carbonates of strontium and calcium are less soluble than the sulphates, while for barium the relation is reversed. From the results already given it is quite simple to find the concentration of $\overset{--}{\mathrm{CO}_3}$ ions necessary to form the carbonate from the sulphate. Thus for barium, by (6) and (11) we find that,

$$x = \frac{0.0000000105}{0.00001} = 0.00115\,;$$

i. e., it is necessary to have a minimum of 0.00105 gram-molecules of CO_3 ions to the liter to cause the solubility product of barium carbonate to be reached in a saturated solution of barium sulphate.

In a like manner we find values of $\overset{--}{\mathrm{CO}_3}$ for strontium and calcium to be :

$\mathrm{CO}_{3(\mathrm{Sr})} = x = \dfrac{0.000000005}{0.00054} = 0.0000092$ normal (by (8) and (13)).

$\mathrm{CO}_{3(\mathrm{Ca})} = x = \dfrac{0.0000000154}{0.054} = 0.000000385$ normal (by (10) and (15)).

These values would not cause the complete transformation of the sulphate into carbonate, but anything over them would cause some of the carbonate to be formed. It must always be borne in mind that an alkali sulphate is formed by the transformation, and that the $\overset{--}{\mathrm{SO}_4}$ ions of this decrease the solubility of the insoluble sulphate so that equilibrium would be reached unless a sufficient excess of $\overset{--}{\mathrm{CO}_3}$ ions are present. The relation between the effect of the $\overset{--}{\mathrm{SO}_4}$ ions, and those of $\overset{--}{\mathrm{CO}_3}$ may be readily calculated. Thus for barium sulphate, the solubility is depressed from 0.00001 normal to 0.000000001 normal by a tenth-normal solution of $\overset{--}{\mathrm{SO}_4}$ ions; *i. e.*,

$$y + 0.1 = 0.0000000001.$$

$$y = 0.000000001 = \text{concentration of } \overset{++}{\mathrm{Ba}} \text{ ions.}$$

The amount of $\overset{--}{CO_3}$ ions necessary to cause the solubility product of the barium carbonate to be reached is then,

$$0.000000001 \times x = 0.0000000105$$
$$x = 10.5 \text{ normal.}$$

In other words a tenth-normal solution of $\overset{--}{SO_4}$ makes it necessary to add an equal amount of a 10.5 normal solution of $\overset{--}{CO_3}$ to cause the solubility product of barium carbonate to be reached, and until that concentration is exceeded no barium carbonate can be formed. The tenth-normal solution of $\overset{--}{SO_4}$ has not such a marked effect upon the formation of the carbonates of strontium and calcium. Thus:

$\overset{++}{Sr} \times 0.1\,\overset{--}{SO_4} = 0.00000029$

$\overset{++}{Sr} = 0.0000029$ solubility of $SrSO_4$ in presence of tenth-normal $\overset{++}{SO_4}$.

$$0.0000029 \times \overset{--}{CO_3} = 0.000000005$$
$$\overset{--}{CO_3} = 0.0017 \text{ normal.}$$

By this it is possible to explain the non-solution of barium sulphate in ammonium carbonate and in a solution of a sulphate and carbonate. In the case of ammonium carbonate acting upon the three sulphates, those of strontium and calcium form rapidly, even though the concentration of the $\overset{--}{CO_3}$ ions is small. The barium sulphate may also dissolve slightly, but the soluble sulphate formed during the reaction will soon prevent any further formation, and that formed from the strontium and calcium salts will cause the reverse transformation to take place, so that the barium sulphate transformed, will be formed again and its solubility decreased in proportion to the amount of $\overset{--}{SO_4}$ ions. Since our object is to make the precipitates as insoluble as possible it is always well to have an excess of the precipitant. According to Fresenius it is advisable to use a solution containing by weight one-third as much sulphate as carbonate. The carbonate and sulphate of potassium will then be related in terms normal as 1 : 0.4; and if we use a normal solution of potassium carbonate mixed with a 0.4 normal solution of potassium sulphate, the relation of the ions of $\overset{--}{CO_3}$ and $\overset{--}{SO_4}$ will be as 0.48 is to 0.21 normal. Absolutely no barium carbonate will then be produced and the solubility of the barium sulphate will be depressed to

$$\overset{++}{Ba} \times 0.21 = 0.0000000001$$

$$\overset{++}{Ba} = 0.0000000005 \text{ normal.}$$

The solubility of the strontium as well as of the calcium sulphate will be depressed but slightly.

$$\overset{++}{Sr} \times 0.21 = 0.00000029$$

$$\overset{++}{Sr} = 0.0000013$$

$$0.0000013 \times \overset{--}{CO_3} = 0.000000005$$

$$\overset{--}{CO_3} = 0.004 = \text{amount necessary to form solubility}$$

product.

$$\overset{++}{Ca} \times 0.21 = 0.0029$$

$$\overset{++}{Ca} = 0.014$$

$$0.014 \times \overset{--}{CO_3} = 0.000000154$$

$$\overset{--}{CO_3} = 0.000011 = \text{amount necessary to form solu-}$$

bility product.

And even with the soluble sulphate formed during the reaction the carbonates will be produced very rapidly. The speed of the transformation will in all cases be proportional to the difference between the concentration of the metallic ions from the carbonate and sulphate. The separation in presence of ammonium carbonate, then, is caused by the soluble sulphate formed during the reaction acting upon the barium sulphate, thus making it more insoluble, while it has practically no retarding effect upon the transformation of the other two sulphates. When one molecule of $\overset{--}{SO_4}$ is present with barium sulphate, it counteracts the influence of 105 molecules of $\overset{--}{CO_3}$. In the case of the mixture of carbonate and sulphate the amount of sulphate has but a slight depressing effect upon the strontium and calcium sulphates, while it depresses, to a very great extent, the solubility of the barium sulphate. The excess of $\overset{--}{CO_3}$ ions has the same effect upon the two carbonates so that the three salts are made as insoluble as possible and are separated by hydrochloric acid, the calcium and strontium being then separated by other reagents.

All the above, as far as concerns the carbonates, is modified slightly by the hydrolytic dissociation which takes place in the solutions. The relations, however, between the carbonates and sulphates will remain unchanged since the hydrolytic dissociation will take place to nearly the same extent in the solutions of all three.

REVIEW.

A BRIEF HISTORY OF THE MOVEMENT FOR INCREASING THE ACCURACY AND FOR IMPROVING THE CONSTRUCTION OF CHEMICAL MEASURING INSTRUMENTS.

The greater part of the matter contained in this paper was compiled for the use of the "Committee on Standards for Chemical Measuring Instruments" of this society and formed a part of that committee's report, which was read at the New York meeting in December last, and which is now before the committee for the reconsideration of some minor details, in accordance with a promise made to a minority of the committee. I may state, however, that the committee has unanimously agreed to the proposition that the society extend a formal invitation to the U. S. Office of Standard Weights and Measures to adopt regulations governing the construction, calibration, and testing of volumetric apparatus, similar to the regulations of the Kaiserliche Normal-Aichungs-Commission of Germany. This was the most important recommendation contained in the report of the committee as presented at New York, and it will soon be before the council of the society for action.

It is at the suggestion of my fellow members of the committee that I now present the following data in this form.

THE WORK OF EUROPEAN CHEMISTS.

As early as 1891, the "Deutsche Gesellschaft für angewandte Chemie" and the "Verein deutschen Eisenhüttenleute" had taken up the question of standards for chemical measuring instruments, and it was with the assistance and coöperation of these associations that the excellent regulations of the German Normal-Aichungs-Commission for testing volumetric apparatus were perfected and finally adopted. These regulations, as published in 1893, were as follows:

NOTICE IN REGARD TO THE TESTING OF CHEMICAL MEASURING FLASKS, ETC.

[From Zeitschrift für angewandte Chemie, 1893, pp. 557-559].

The Kaiserliche Normal-Aichungs-Commission published the following directions, based upon article 18 of the regulations governing weights and measures (special supplement to Reich's Gesetzblattes, No. 30):

I. ALLOWABLE MEASURING APPARATUS.

1. For exclusive use for chemical volumetric analysis of aqueous solutions, glass vessels will be admitted for testing as follows:

Vessels with one mark to hold a single volume.

(*a*) Flasks.

(*b*) Pipettes with upper suction tube and a lower delivery tube.

Vessels marked to hold a certain definite volume and certain subdivisions thereof.

(*c*) Measuring glasses (also called measuring cylinders, being measuring tubes having a foot).

(*d*) Burettes (measuring tubes without a foot, but with a delivery tube).

(*e*) Measuring pipettes (measuring tubes having a suction tube at the upper end and a delivery tube at the lower end).

2. The capacity of a measuring vessel is to be limited either by the mark or the lower opening, and its quantity is marked upon the vessel for a temperature of a vessel of 15° of the centigrade thermometer, in the liter, fractions of a liter, or in cubic centimeters, in which case the cubic centimeter is to be the 1-1000 part of a liter.

3. Measuring vessels may be graduated either to hold (*messgeräthe auf Einguss*) a given quantity to the mark, or to deliver (*messgeräthe auf Ausguss*) a given quantity. Measuring vessels provided with a device for the delivery of liquids must always be graduated to *deliver* the volume of liquid for which they are marked. Other vessels may be graduated to either hold or to deliver, but for only one of these purposes in the case of any single vessel. The volume of liquid is measured with a delivery apparatus by filling and emptying, with precautions to retain a uniformly unpreventable moistening of the walls of the vessel. This uniform moistening is insured by observing the following precautions:

(*a*) Measuring vessels which are emptied by turning up-side-down are held for one minute after emptying in an inclined position to allow them to drain, when the last drop is wiped off.

(*b*) In the case of pipettes the liquid is allowed to flow out entirely, or to the lower mark, according to the method of graduation, while the delivery tube is held without motion in contact with the sides of the receiving vessel. After the free outflow of the liquid has stopped, or after the lower mark has been reached, the pipette is allowed to drain for one-quarter of a minute.

(*c*) In the case of burettes, or measuring pipettes (pipettes graduated to deliver fractions of their maximum capacity), the desired quantity is drawn out, the last drop is removed, and the reading is taken off after waiting two minutes.

4. The cross-section of the measuring vessel must always be circular. The space occupied by the liquid to be measured, viewed in the direction of its greatest diameter, should decrease in size above and below, best at the same rate. Where the body of the vessel has a tube or cylindrical portion sealed on, the body of the vessel must gradually merge into the cylindrical portion without any abrupt change of direction, so that there will be no hindrance to the ready outflow of the liquid.

5. The mark shall be narrow, and both it and the label shall be plainly etched, ground, or applied in some other permanent manner. It should never be merely painted. The mark should always be upon a cylindrical, regularly formed, transparent part of the vessel. Coloring the mark is permitted.

6. The mark shall pass at least halfway around the vessel and lie in the plane to which the axis of the vessel is perpendicular.

7. In the case of measuring vessels marked for subdivisions of their total capacity, these subdivisions must all be equal.

8. Capacity of a flask may be stated in liters or cubic centimeters (the mark being *liter*, *l.*, or *cc.*), while all other vessels may be marked only cubic centimeters—*i. e.*, with the mark *cc.* The mark expressing the capacity of a vessel without subdivisions, is placed on the middle part of the body of the vessel.

9. The numbers of the marks on vessels marked for subdivisions of their total capacity, are to be placed at the right end of the lines denoting cubic centimeters as units. These numbers must run consecutively and in only one direction; *i. e.*, either from the top down or from the bottom up.

The "cc." mark is added to the line bearing the largest number, whether it be at the beginning or at the end of the graduation.

10. There must be etched below the mark indicating the capacity, in the case of flasks and other vessels having but one graduation mark, the expression +15° C., indicating the temperature at which the capacity of the flask is equal to the volume indicated by its label. In the case of instruments graduated for fractions of their total capacity, this mark (+15° C.) is etched at least 15 mm. above the graduation. There must also be placed at the left of this mark and at the same height the mark *E.* or *A.*, *Eing.* or *Ausg.*, *Einguss* or *Ausguss*, as the case may be, to indicate whether the instrument has been graduated to hold or to deliver the volume of liquid indicated by its label.

A manufacturer's number, name, and address, and a trade mark may be placed opposite the label mentioned above on the other side of the flask. In the case of apparatus graduated for subdivisions the manufacturer's marks are to be placed in long lines at the left of the graduation.

11. In the case of all measuring vessels the reading shall be taken at that point of the wall of the vessel where it is cut by the plane which is perpendicular to the axis of the vessel and at the same time tangent to the meniscus of the liquid at its lowest point.

12. Inflow and outflow tubes, stoppers, etc., must not end in the measuring space of the vessel or extend therein. The limiting of the measuring space directly by cocks is inadmissible. Beyond the part actually occupied by the liquid to be measured the vessel may be provided with cocks, tubes, expansions made of irregular form, etc., *ad libitum*.

13. In the case of measuring vessels having a delivery tube or point, the latter should be drawn out as thin as stability will permit. and its termination should be smooth and even. It is permissible to constrict the orifice somewhat. In the case of burettes of the Gay-Lussac form, the delivery point should be bent back toward the delivery tube, and should be ground obliquely on the under side.

II. Measuring Vessels without Minor Graduation.

(Flasks and pipettes graduated to deliver one maximum volume).

1. Flasks may be made of the following capacities: 2, 1, ½(0.5), ¼(0.25), 0.2, 0.1, and 0.05 liter; pipettes, of any desired capacity from 1 to 200 cc.

2. In the case of both forms of apparatus the part bearing the graduation mark must be cylindrical (see above, I, 5), of uniform section, and transparent. Moreover, this cylindrical portion must pass over very gradually into the expanded part of the apparatus.

3. In the case of pipettes the suction tubes must be at least 130 mm. long, and the delivery tubes at least 60 mm., but not more than 300 mm. long.

4. The graduation mark must be at least 70 mm. from the upper end of the neck of a flask, and in the case of a pipette at least 100 mm. from the upper end and at least 30 mm. from the bulb. The mark must extend entirely around the neck of the flask or the suction tube of the pipette.

5. At the point where the graduation mark is placed the internal diameter of the neck of the flask shall not be less than 6 mm., and shall not exceed the following maximum figures given for flasks of each of the sizes admitted for testing:

Capacity of flask. Liters.	Maximum internal diameter of neck. mm.
2	25
1	20
½(0.5)	20
¼(0.25)	15
0.2	12
0.1	12
0.05	10

In the case of pipettes the suction and delivery tubes must have an internal diameter of not less than ½ mm. and not more than 6 mm.

6. The bottom of the flask may be slightly reentrant. The circumference of the bottom of the flask must form a plane to which the neck of the flask is perpendicular. The flask must stand solidly on a horizontal surface.

7. The lower limit of the volume of a pipette may be either the end of the delivery tube or a second mark etched thereon at least 30 mm. from the end.

In the case of pipettes without a cock, the delivery orifice must be of such a size that the discharge of the pipette, conformable to I, 3, (*b*), lasts:

12 to 15 seconds when the pipette is of less than 10 cc. capacity.

15 to 20 seconds when the capacity of the pipette is of 10 cc. or more but less than 50.

20 to 30 seconds when the capacity of the pipette is 50 cc. or more but less than 100.

30 to 40 seconds when the capacity of the pipette is 100 cc. or more.

In the case of pipettes provided with cocks, the testing must be made for that setting of the cock which requires the following time for emptying the pipette:

13 to 17 seconds when the capacity of the pipette is less than 10 cc.

16 to 20 seconds when the capacity of the pipette is 10 cc. or more but less than 50.

23 to 27 seconds when the capacity is 50 cc. or more but less than 100.

33 to 37 seconds when the capacity of the pipette is 100 cc. or more.

III. MEASURING VESSELS WITH MINOR DIVISIONS.

1. The total volume of vessels graduated for subdivisions thereof may have any value between 1 cc. and 1 liter, but for cylinders and burettes shall not be less than 5 cc., and for burettes and pipettes not more than 100 cc.

2. The subdivisions permitted are as follows:

When the total capacity of the apparatus is 1 cc. and up to and including 2 cc., the smallest subdivision is 0.01 to 0.02 cc.

When the total capacity of the apparatus is more than 2 and up to and including 5 cc., the smallest subdivision is 0.05 to 0.02 cc.

When the total capacity of the apparatus is more than 5 and up to and including 10 cc., the smallest subdivision is 0.05 to 0.1 cc.

When the total capacity of the apparatus is more than 10 and up to and including 50 cc., the smallest subdivision is 0.1 to 0.2 cc.

When the total capacity is more than 50 and up to and including 100 cc., the smallest subdivision is 0.2, 0.5, or 1 cc.

When the total capacity is more than 100 and up to and including 200 cc., the smallest subdivision is 1, 2, or 5 cc.

When the total capacity is more than 200 and up to and including 500 cc., the smallest subdivision is 5 to 10 cc.

When the total capacity is more than 500 cc., the smallest subdivision is 10 cc.

3. The measuring space may be limited by lines below as well as above. In the case of pipettes, the upper graduations must be at least 100 mm. from the upper end of the apparatus and at least 50 mm. in other cases. The lower mark of the graduation, in cases where the bottom of the vessel is not the lower limit of the graduation, must be at least 30 mm. from the lower end of the apparatus or from the beginning of the contraction of the body thereof.

4. The numbering is to be done as follows:

(*a*) In case of division into 10, 1, 0.1, or 0.01 cc., every tenth mark is numbered.

(*b*) In case of division into 2, 0.2, or 0.02 cc., every fifth line is marked.

(*c*) In case of division into 5, 0.5, or 0.05 cc., every second or tenth line is marked.

The numbered lines must extend entirely around the vessel. Of the other lines, the fifth in the case "a" and whenever only every tenth line is numbered, and the first line when every second line is numbered, must extend three-fifths of the way around the vessel, while all other lines extend only one-half way around.

All lines not passing entirely around the vessel must be on transparent glass; any opaque strips for facilitating the reading of the instrument must not be greater in breadth than two-fifths of the circumference of the tube.

5. The distance between two consecutive division marks must not be more than 12 mm., and for measuring cylinders graduated for each 5 cc. or more, not less than 2 mm., while for all

other measuring vessels this distance must not be less than 1 mm.

IV. LIMIT OF ERROR.

1. Measuring vessels without divisions.

For flasks graduated for delivery the error must not exceed the following limits:

Capacity. Liters.	Allowable error. cc.
2	1
1	0.6
0.5	0.3
0.2	0.2
0.1	0.2
0.05	0.1

For flasks graduated to hold the quantities of liquid just named, the allowable error is one-half as great in each case.

For pipettes delivering only maximum quantity, the allowable errors are as follows:

Capacity of pipette. cc.	Allowable error. cc.
1 to 2	0.01
More than 2 to 10	0.02
More than 10 to 30	0.03
More than 30 to 75	0.05
More than 75 to 200	0.1

2. Measuring vessels with divisions—burettes and pipettes.

Maximum capacity. cc.	Allowable error on maximum capacity. cc.
1 to 2	0.01
More than 2 to 10	0.02
More than 10 to 30	0.03
More than 30 to 50	0.05
More than 50 to 100	0.1

In the case of graduated cylinders of the dimensions just given, the allowable error is double that for burettes and pipettes when the instruments are graduated to hold a certain volume, but four times as great as the errors allowed for burettes and pipettes when graduated for delivery or pouring out.

For larger measuring cylinders graduated to hold definite volumes, the allowable errors are as follows:

Maximum capacity. cc.	Allowable error. cc.
More than 100 to 200	0.5
More than 200 to 500	1
More than 500	2

When graduated for delivery or pouring, the allowable errors are just twice as great.

For measuring cylinders graduated to hold a definite volume, the maximum errors for the volumes indicated by ten of the consecutive smallest divisions must on no part of the graduation be greater than as shown below.

1 cc. when the divisions equal 10 or 5 cc.
0.4 cc. when the divisions equal 2 cc.
0.2 cc. when the divisions equal 1 or 0.5 cc.
0.1 cc. when the divisions equal 0.2 or 0.1 cc.

In the case of cylinders graduated for delivery, double these errors are allowed. In the case of burettes and pipettes graduated to 0.01 to 0.2 cc., the error must not be greater than one-third of the smallest division, and not more than one-fourth of the smallest division in other cases.

V. STAMPING.

The official stamp is etched upon flasks immediately over the graduation mark and also over the label. On pipettes graduated to deliver one maximum volume the official stamp is etched immediately over the upper mark and immediately under the lower mark, when there is one.

In the case of other measuring vessels the official stamp is placed close above the upper mark and close below the lower one; besides this, the stamp is also placed on the delivery tube, close to its end.

VI. FEES FOR TESTING.

The fees are as follows:

(*a*) For testing and placing the official stamp on measuring vessels without divisions, 30 *pf.* ($0.072).

Measuring vessels having divisions, 80 *pf.* ($0.192).

(*b*) For mere testing, for each complete volume or each mark tested, 10 *pf.* ($0.024).

If a vessel having divisions is tested for more than 5 marks besides the one indicating the total volume, each additional mark tested is charged for at the rate given under *b*.

VII. PLACE OF TESTING.

The testing and stamping of measuring vessels will be done by the Normal-Aichungs-Commission until further notice.

KAISERLICHE NORMAL-AICHUNGS-COMMISSION, HUBER.
BERLIN, July 26, 1893.

Supplemental regulations were adopted by the Aichungs-Commission in 1897 as follows:

ADDITIONAL REGULATIONS FOR THE TESTING OF CHEMICAL MEASURING INSTRUMENTS, ADOPTED BY THE KAISERLICHE NORMAL-AICHUNGS-COMMISSION, JULY 2, 1897.

[Zeitschrift für angewandte Chemie, (*1897*), 643–647; Zeitschrift für analytische Chemie, (*1898*), 37, Amtliche Verordnungen und Erlasse, 2–6.]

I. ADDITIONAL FORMS OF APPARATUS ADMITTED FOR TESTING.

In addition to the forms of measuring instruments for exclusive use for chemical analysis of aqueous solutions, mentioned in the notice of July 26, 1893,[1] the following forms will now be accepted for testing:

a. For use in sugar analysis, flasks with two marks and flasks with one mark, or with two marks for a temperature of 20° (Section II).

b. Flasks for use with viscosimeters with two marks for a temperature of 20° (Section III).

c. Flasks with capacities of 150, 300, 350, 400, 450, 550, 600, 650, 700, 750, 800, 850, and 950 cc. (Section IV).

d. Measuring vessels with incomplete graduation (section V).

e. Overflow pipettes (Section VI).

The forms of apparatus mentioned under *a* to *e* shall meet the requirements of the regulations announced July 26, 1893, in so far as the paragraphs here following do not conflict therewith.

II. FLASKS FOR SUGAR ANALYSIS.

1. These flasks must be graduated to hold the volumes indicated by their labels, and may have capacities of 50, 100 or 200 cc. A second mark may be placed above the one which marks the limit of the capacity of the flask. These two marks must be separated at least 10 mm. in the case of 50 and 100 cc. flasks; and at least 30 mm. in the case of 200 cc. flasks.

Between the two marks the neck of the flask may be enlarged, provided that it is cylindrical for at least 3 mm. above the lower mark and for at least 3 mm. below the upper mark. The capacity limited by these two marks must not be greater than the tenth part, nor less than the two-hundredth part of the capacity of the flask as limited by the lower mark.

2. Besides the label *E*, or *Eing*., or *Einguss*, the standard temperature, +15° C. or +20° C., shall be etched upon the flask (Section 1, 10, of the regulations of July 26, 1893). The label indicating the capacity of the flask must be etched upon the body of the flask; and, in the case of flasks with two marks, must denote the capacity of the flask as limited by the lower mark. Flasks with two marks must have, in addition, a label etched midway between the two marks and indicating the capacity of

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[1] *Reichs-Gesetzblatt*, Beilage No. 30.

the space included between them, stated in cc. or in fractions of a liter.

3. The internal diameter of the neck of the flask must not be greater than 10 mm. for 50 cc. flasks; not greater than 12 mm. for 100 cc. flasks; and not greater than 25 mm. (15 mm?)[1] for 200 cc. flasks.

4. In the case of flasks with two marks, the upper mark must be at least 50 mm. from the upper end of the neck; in the case of flasks with one mark, the mark must be at least 50 mm. from the upper end of the neck for 50 and 100 cc. flasks, and at least 70 mm. for 200 cc. flasks.

5. The limits of error prescribed by Section IV, 1, of the regulations of July 26, 1893, for flasks graduated to hold 50, 100, and 200 cc. must not be exceeded by sugar flasks of the same respective capacities.

In the case of flasks with two marks, the limit of error of the volume included between the two marks is one-half of that permitted for the entire capacity of the flask.

6. The stamping is to be done in the manner prescribed for flasks at present admitted for verification. In the case of flasks with two marks, however, a second stamp is to be placed above the upper mark. The stamp for the lower mark may be etched directly under the lower mark.

7. The fees will be, in addition to the regular fee of 10 *pf.* for each piece of apparatus presented for verification:

a. For testing and stamping flasks:

Flasks with one mark, 40 *pf.* ($0.096);
Flasks with two marks, 60 *pf.* ($0.144).

b. For mere testing:

For each mark tested, 10 *pf.* ($0.024).

III. Flasks for Viscosimetry.

1. These flasks are only to be graduated to deliver the volumes indicated by their labels; and are to be made only with two marks, one for 200 cc. and one for 240 cc. Between the two marks the neck of the flask may be expanded in the form of a bulb, but it must still be cylindrical for at least 3 mm. above the lower mark and for the same distance below the upper mark.

2. The internal diameter of the neck must not exceed 20 mm. at either mark.

3. In addition, the requirements of Section II, paragraphs 2 and 4 to 7 must be fulfilled with the restriction that the label is to be *A*, or *Ausg.*, or *Ausguss*, and + 20° C.; and the limits of error are to be those of flasks graduated for pouring out.

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[1] In the regulations as copied in *Ztschr. angew. Chem.*, this number is 25 mm., while in *Ztschr. anal. Chem.* it is 15 mm. See references above.

IV. OTHER FLASKS.

In view of the additional forms of apparatus admitted for testing by Section I, *c*, the regulations of July 26, 1893, in so far as they refer to flasks, are amended as follows:

Section II, 5. At the point where the graduation mark is placed, the internal diameter of the neck must not be less than 6 mm., and must not be greater than 10 mm for 0.05 l. flasks; not greater than 12 mm. for 0.1 to 0.2 l. flasks; not greater than 15 mm. for 0.25 to 0.45 l. flasks; not greater than 20 mm. for 0.5 to 1 l. flasks; and not greater than 25 mm. for 2 l. flasks.

Section IV, 1. The positive or negative error for flasks graduated for delivery must not exceed 1 cc. for 2 liter flasks; 0.6 cc. for flasks delivering from 1 to and including 0.55 liter; 0.3 cc. for flasks delivering from 0.5 to 0.3 liter; 0.2 cc. for flasks delivering 0.25 to 0.1 liter; and 0.1 cc. for 0.05 liter flasks.

In the case of flasks graduated to hold the volumes named, the respective limits of error must not exceed half the amounts named.

V. MEASURING VESSELS WITH INCOMPLETE GRADUATION.

1. The lowest marks of these instruments, which may or may not be provided with a foot, limits an unsubdivided cylindrical or bulb-shaped space having a capacity of a certain number of whole cc.

2. When this lower space is bulb-shaped, that portion of it extending downward from the graduation mark must be cylindrical for at least 15 mm.

If the vessel is enlarged above the upper mark, the enlargement must begin at least 30 mm. from the upper mark.

3. The graduation of these vessels shall be done in the manner described for measuring glasses of forms previously admitted for testing, in accordance with which the number placed opposite the lowest mark indicates the capacity of the ungraduated part. In determining the graduation permissible (Section III, 1 and 2, of the regulations of July 26, 1893), the space included between the upper and lower marks is to be considered the total capacity, but neither this space nor the lower ungraduated space may exceed 100 cc.

4. The stamp placed underneath the lowest mark attests also the accuracy of the ungraduated portion.

VI. OVERFLOW PIPETTES.

1. Overflow pipettes are pipettes whose capacities are limited above by the end of the upper tube instead of by a mark placed

thereon. The apparatus may be otherwise constructed like ordinary pipettes, the filling being done by means of the delivery tube; or a special tube for the entry of the liquid to be measured may be provided, both the inflow and outflow tubes being controlled by the same cock.

2. The end of the upper tube must be even; its internal diameter must not be greater than 3 mm. in the case of pipettes delivering 500 cc. or less, and not greater than 5 mm. in the case of pipettes of larger capacity. The upper tube must not be longer than 75 mm.; the lower tube not longer than 150 mm. Overflow pipettes may have any capacity between 1cc. and 2000 cc.

3. The time of emptying of overflow pipettes delivering from 1 to 200 cc. must be the same as the time prescribed for ordinary pipettes of the corresponding capacity; for pipettes delivering more than 200 cc. to 500 cc., the time of delivery must be 55 to 65 seconds; for pipettes delivering more than 500 cc. to 1000 cc., 110 to 130 seconds; and for pipettes delivering more than 1000 cc., 170 to 230 seconds (200 seconds?).[1]

4. The limits of error allowable for overflow pipettes of capacities from 1 cc. to 200 cc. are those prescribed for ordinary pipettes of the corresponding capacities; for pipettes delivering more than 200 cc. to 500 cc., the limit of error allowable is 0.2 cc.; for pipettes delivering more than 500 cc. to 1000 cc., 0.3 cc.; for pipettes delivering more than 1000 cc. to 2000 cc., 0.5 cc.

5. There shall be placed upon overflow pipettes at least three stamps. One of these shall be placed over the label, the second one immediately below the upper end of the upper tube, and the third one on the outflow tube close to its end.

In case the capacity of the pipette is limited below by a mark on the outflow tube, a fourth stamp must be placed immediately under the mark.

6. In addition to the regular fee of 10 *pf.* ($0.024) for each piece of apparatus presented for verification, the charges for testing, stamping, etc., will be as follows:

a. For testing and stamping

Overflow pipettes delivering 200 cc. or less, 40 *pf.* ($0.096);

Overflow pipettes delivering more than 200 cc., 60 *pf.* ($0.144).

b. For mere testing

Overflow pipettes delivering 200 cc. or less, 10 *pf.* ($0.024);

Overflow pipettes delivering more than 200 cc., 30 *pf.* ($0.072).

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[1] The statement in the *Ztschr. angew. Chem.* is 230 seconds; in the *Ztschr. anal. Chem.*, 200 seconds

VII. PLACE OF TESTING.

The testing of all forms of measuring instruments named will be done by the Normal-Aichungs-Commission or at the places designated for the testing of chemical measuring instruments in Article 1, Section VII of the notice of April 8, 1896 (Reichs-Gesetzbl. 1896, Beilage zu No. 9).

VIII.

1. The regulations of July 26, 1893, Section II, 4, are hereby amended so that 50 cc. and 100 cc. flasks are allowable with the graduation mark at least 50 mm. from the upper end of the neck.

2. Under Section III, 2, of the regulations of July 26, 1893, the following additional forms of apparatus are provided for:

Instruments having a total capacity of 5 cc. and graduated in 0.1 cc. divisions; and instruments having a total capacity of 10 cc. and 0.02 cc. (0.2 cc?) divisions.[1]

3. The requirements of Section IV, 2, of the regulations just mentioned are amended as follows:

Moreover, the positive or negative error allowable for the capacity limited by each mark, or between two marks must not be greater than one-half of the error permitted for the entire capacity of the instrument, in case the fractional capacity in question is less than one-half the total capacity; and the error of a fractional capacity equal to or greater than one-half of the total capacity of the instrument must not exceed the error permitted for the total capacity.

The graduation must also appear regular to the eye. In no case may adjacent smallest divisions differ from each other by more than one-fourth of the distance between the lines limiting each of these smallest divisions.

REGULATIONS FOR THE TESTING OF INSTRUMENTS FOR DETERMINING THE PERCENTAGE STRENGTH OF SUGAR SOLUTIONS.

I. There shall be admitted for testing glass thermo-saccharimeters which indicate the temperature in degrees of the centigrade thermometer, and, at a temperature of +20°, the per cent. by weight of sugar contained in pure sugar solutions.

The thermometer scale of the instrument must be divided in whole or in half degrees. When the percentage scale is divided in whole or in half per cent., the thermometer shall be divided in whole degrees and otherwise in half degrees.

The entire length of the divisions of a percentage scale must not exceed 200 mm.; the length of its smallest subdivisions must be at least 1 mm.

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[1] The statement in the *Ztschr. angew. Chem.* is 0.02 cc.; in the *Ztschr. anal. Chem.*, 0.2 cc.

Thirty per cent. shall be regarded as the normal range for each instrument. Hence, three kinds of instruments will be necessary: 0 to 30 per cent.; 30 to 60 per cent.; and 60 to 90 per cent. Instruments with scales of other ranges are, however, allowable. Instruments with 0.1 per cent. subdivision must not have a greater range than 20 per cent.

The thermometer scales must be made for a range of temperature from 0° to +35°. In the case of instruments graduated for whole or half per cent., the thermometer scale may be extended to 70°. The length of the smallest subdivision of the thermometer scale must be at least 1.5 mm.

II. 1. The loading of the instrument, necessary for maintaining its vertical position when floated in the solution, shall be supplied by the bulb of a thermometer.

Material for making the final adjustment of the instrument may be placed on the inside of the scale, but it must be of such a nature as to make it impossible for it to become loosened by external force or because of its own properties.

2. The outer surface of the instrument shall be regular and symmetrical with respect to its axis; its proportion shall be such that it assumes a perpendicular position when floated in a liquid.

3. The top of the spindle shall be regularly rounded and have a smooth surface with no depressions or ridges which may hinder the stamping of the instrument.

The external diameter of the body of the instrument must not exceed 28 mm., and that of the spindle must not be less than 4 mm. nor more than 7 mm.

The capillary tube of the thermometer must have no expansion above the scale, and shall only be of such length that the instrument may be heated to 75° C. without danger of breaking.

4. The paper scale must be fastened to the glass wall of the instrument in a permanent manner. Cements which loosen on warming are not permissible.

5. The upper end of the percentage scale shall be at least 15 mm. below the upper end of the spindle.

The upper end of the thermometer scale shall be at least 20 mm. below the place where the glass body of the instrument begins to contract.

6. Upon the percentage scale, in the case of division in whole per cent., the marks for the fifth and tenth per cent. shall be numbered and shall be longer than the others. In other cases the mark for each whole per cent. shall be numbered. In case of divisions for each 0.1 per cent., the marks for each half per cent. shall be longer than the other marks. The shortest marks shall extend at least one-fourth of the way around the spindle.

On the thermometer scale the marks shall run in uninterrupted course and shall be visible on both sides of the capillary tube; those for each fifth degree shall be longer, and those for each one-half degree shall be shorter than the others.

Each tenth degree shall be numbered.

The numbering of the marks and also the labeling of the scales shall be readily legible.

7. The per cent. scale shall extend into the expansion of the spindle leading into the body of the instrument, but shall not extend into the latter; it may, however, only bear marks so far as the spindle is cylindrical.

The marks of the thermometer scale may extend downward to within 2 mm. of the bend in the capillary tube.

8. The scales must not have appreciable error of division; adjacent subdivisions must not differ from each other by more than one-fourth of their mean length.

III. The thermometer scale shall bear the label "Degrees of the centigrade thermometer"; and the percentage scale, the label "Percentage-by-weight saccharimeter" ("*Saccharimeter nachs Gewichtspercenten*").

A manufacturer's number shall be placed at the upper end of the thermometer scale.

It is permissible to place the name and address of the manufacturer, and also the date of manufacture on one of the scales, but nothing additional may be placed thereon.

IV. The positive or negative errors permissible are as follows, according as the minor divisions of the percentage scale are for

	1 per cent.	1/2 per cent.	1/5 or 1/10 per cent.
On the thermometer scale ...	0.4°	0.4°	0.2°
On the saccharimeter scale ..	0.5 per cent.	0.25 per cent.	0.1 per cent.

The reading of the thermometer in melting ice must not undergo a greater alteration on heating to the highest temperature of the scale than one-fourth of the limit of error given above for the class of instruments to which it belongs.

On the percentage scale the reading is to be taken at the point where the plane of the surface of the liquid cuts the scale.

V. The official stamp, together with a number and the date shall be etched on the body of the instrument above the thermometer scale. A small stamp shall also be placed at the top of the spindle.

The weight of the instrument in milligrams shall be etched upon the body of the instrument.

Upon the spindle, immediately over the upper end of the percentage scale and immediately below the lowest mark thereof, marks shall be placed which extend at least half way around the spindle. The lower side of the upper mark shall lie in the plane of the edge of the scale, and the upper side of the lower mark shall be in the plane of the lowest mark of the scale.

VI. In order to obtain true percentage readings the official table of the Normal-Aichungs-Commission must be used.

VII. The following fees have been fixed :

a. For testing and stamping
Each thermo-saccharimeter, 2 *Marks* ($0.48).

b. For mere testing
Of the thermometer scale, 10 *pf.* ($0.024) ;
Of the percentage scale, 25 *pf.* ($0.060).

If more than five points of either scale are tested when an instrument is submitted for testing and stamping, each additional place tested will be charged for at the rates given under *b*.

VIII. The testing of thermo-saccharimeters will be done by the Normal-Aichungs-Commission or by *Aichämter* designated by the Normal-Aichungs-Commission.

KAISERLICHE NORMAL-AICHUNGS-COMMISSION, HOPF.
BERLIN, July 2, 1897.

This act of the Aichungs-Commission, done five years ago, made it comparatively easy for German chemists to obtain volumetric apparatus of known form of construction and of known accuracy. A flask and a burette, tested in accordance with these regulations and bearing the official stamp of the Aichungs-Commission were exhibited at the Boston meeting of this society.

At the International Congress of Applied Chemistry, held in Brussels, in 1894, the question of uniform methods for the analysis of commercial products was discussed, and very naturally the question of international standards for measuring instruments came up at the same time. The following resolutions were adopted unanimously and an international committee was appointed to continue the work and report at the next congress.

"1. The International Congress of Applied Chemistry adopts as the international unit for the graduation and calibration of chemical apparatus, the metric liter and its decimal subdivisions.

"2. It is of the opinion that the centigrade, or Celsius, thermometer should be used to the exclusion of all others.

"3. An international commission, composed of members elected by the congress, shall be entrusted with the duty of determining the conditions of graduation, of testing, and for using chemical apparatus, particularly flasks, burettes, pipettes, and hydrometers of various sorts. This commission shall also fix the temperature at which these instruments shall be graduated. It shall elaborate a table showing the degrees Baumé, Brix, Balling, Vivien, etc., which are equivalent to the various indications of the specific gravity hydrometer ; and shall prepare a table showing the corrections which are to be applied to the readings of various forms of hydrometers, when these readings are made at other than standard temperatures."[1]

Preparatory to taking part in the work of the Second International Congress of Applied Chemistry, held in Paris in 1896, the Verein deutscher Chemiker appointed a committee to meet with representatives of the Aichungs-Commission and draft a statement of the German view of the question of standards for chemical measuring instruments.

A. Schmidt, of Cologne, was chosen to present the statement at the Paris congress, as the representative of the Verein deutscher Chemiker, and Prof. Weinstein attended the congress as the representative of the Aichungs-Commission.[2]

This report of the German Committee, changed to accord with the resolutions adopted by the Paris Congress, reads as follows:

PROPOSED REGULATIONS FOR THE CONSTRUCTION AND GRADUATION OF HYDROMETERS AND CHEMICAL MEASURING APPARATUS.

[Zeitschrift für angewandte Chemie, 1896, 603–607.]

A. General Considerations.

1. The unit of volume shall be the true liter and its decimal subdivisions.

2. The basis for the comparison of specific gravities (densities) shall be pure water at 4° and under normal pressure.

3. All weight determinations shall be reduced to weights *in vacuo* by use of Regnault's tables.

4. Temperature shall be expressed in degrees of the centigrade hydrogen thermometer of the International Bureau of Weights and Measures.

5. For the normal temperatures for hydrometers and chemical measuring vessels, 0°, 15°, 17.5° or 20° of the above-mentioned thermometer scale may be chosen. Tables shall be prepared by an international commission for the correction of readings to the normal temperatures.

6. Hydrometers and chemical measuring vessels shall be constructed from glass which possesses the greatest possible resistance to the action of the liquids measured. Each instrument must bear a label showing its normal temperature and unit of volume or specific gravity.

7. The length of the intervals between the marks for the smallest subdivisions of the scales of the instruments shall in all cases be greater than 1 mm.

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[1] Compte-rendus du congres international de chimie appliqué, Bruxelles-Anvers, 4-11 aout, 1894, pp. 205-206.

[2] *Ztschr. angew. Chem.* (*1896*), 406, 602; (*1897*), 519.

8. In making readings at the level of a liquid, consideration must be given to the variation in the phenomena of capillarity.

9. The stems of hydrometers and the graduated parts of measuring vessels must not vary greatly from the cylindrical form.

10. The testing of hydrometers and chemical measuring vessels may be made by comparing them with carefully wrought standards, or by means of the proper weight determinations.

11. In using hydrometers and chemical measuring instruments, the same rules and methods of procedure should be followed as were used in standardizing the instruments.

B. SPECIAL REQUIREMENTS.

(*a*) *Hydrometers.*

1. The scales of hydrometers may be graduated in units of specific gravity, or of the scales of Baumé, Brix, Balling, etc. For the conversion of the readings of arbitrary scales to the equivalent specific gravity, tables shall be prepared by an inter. national commission.

2. For liquids of various capillary properties, special hydrometers shall be used, each graduated for measuring a certain liquid. Each instrument must bear a label showing for what liquid, or group of liquids of similar capillary properties, it has been graduated. The use of the same instrument for solutions of widely different capillary properties is allowable, if the proper corrections be applied to the readings.

3. Hydrometers shall be read, as a rule, at the point where the plane of the surface of the liquid cuts the stem of the instrument, without regard to the meniscus formed by capillarity. In the case of non-transparent liquids, the readings of a hydrometer which has not been graduated for working under such conditions, must be corrected to the true level of the liquid.

4. Hydrometers shall generally be provided with centigrade thermometers, whose scale shall include the zero point.

5. In order to render it certain that the position of the scale within the instrument does not change, a mark shall be placed on the stem in such a position as to be just opposite one of the limiting marks of the scale when the latter is in its correct position.

6. The maximum limit of positive or negative error of a hydrometer shall not exceed, in general, the smallest division of its scale.

(*b*) *Chemical Measuring Vessels.*

(The regulations recommended under this head are not essentially different from those of the Kaiserliche Normal-Aichungs-Commission, as given above.)

Francois Dupont read an elaborate report before the Paris congress, as the representative of the committee appointed by the Brussels congress, in the course of which he stated that no meeting of the committee had ever been held. The subject discussed by the congress seems to have been principally that of a standard temperature. A. Schmidt, of Cologne, asked that the question of temperature be left open until the Vienna congress. After a lengthy discussion, participated in principally by Belgian and French chemists, the president suggested a resolution adopting four temperatures, 4°, 15°, 20°, and 30°, with 4° as a reference temperature, and recommending correction tables for each of the four temperatures. This resolution was unanimously adopted.

The resolutions adopted relative to standards for chemical measuring instruments, as published in the official report of the congress, Vol. 5, pp. 227–228, were as follows:

"1. The unit of volume is the metric liter and its decimal subdivisions.

"2. The specific gravity of liquids is to be referred to 4° C., consequently, hydrometers must be graduated in such a manner that they read 0 or 1.000 when floated in distilled water having a temperature of 4° C.

"3. Tables for comparison of specific gravity with the different hydrometric and saccharometric degrees (Baumé, Brix, Balling, Vivien, Brix-Dupont, etc.), shall be prepared by an international commission. Tables of this sort shall be made for temperatures of 4°, 15°, 20°, and 28° C.

"Tables of corrections shall be prepared by the same commission for temperatures other than those just mentioned.

"4. All weighings shall be reduced to weights in vacuo by means of the tables deduced from the experiments of Regnault.

"5. Temperature should be expressed in degrees of the centigrade hydrogen thermometer, adopted by the International Committee of Weights and Measures.

"All other questions relating to the conditions of construction, graduation, calibration, verification, and reading of chemical measuring instruments shall be referred to the international commission.

"6. The international commission, charged with the duty of preparing tables for the comparison and correction of hydrometer readings, and of establishing regulations for standard measuring instruments, shall be composed of two subcommissions, one French and the other German. The two subcommissions shall communicate with each other and enlist the services of such delegates to the congress as care to participate in the work."

The establishment of uniform and well-defined standards for chemical measuring instruments was thus heartily approved by the

Paris congress; certain general standards were adopted as landmarks; and two commissions were created for carrying out the details of formulating international standards.

The German commission was especially active during the interim between the Paris and Vienna congresses, and presented an elaborate report at the latter, being represented by Prof. Weinstein. The recommendations for standards presented at the Paris congress by Schmidt, as the representative of the Verein deutscher Chemiker, were taken up paragraph by paragraph by the Vienna congress and adopted after slight alterations. Prof. Weinstein announced progress on the preparation of tables for the density of sugar solutions, acids, mineral oils, etc., at various temperatures, and samples of the tables were presented. These tables will be published privately.

The French commission, through its president, Démichel, presented an essentially concurrent report.

The definition of the relation of Baumé degrees to specific gravity was left to the commissions, which were continued.

A prominent auxiliary feature of the Vienna congress, and one of direct interest in this connection, was the second meeting of the International Commission on Uniform Methods of Sugar Analysis. The work of this commission is especially interesting, in view of the controversy now in progress between the U. S. Treasury Department and certain importers of sugars. This litigation involves the regulations governing the testing of sugars and is an excellent illustration of our need of well-defined legal standards for all forms of chemical measuring instruments. At the meeting of the International Commission just mentioned, the United States was represented by Drs. Wiley and Wiechmann. The work of the commission on the comparison of standard quartz plates, and the influence of temperature on the specific rotation of sucrose, were among the more important topics discussed; but, from our present point of view, the agreement of the commission to discard the Mohr flask, in favor of the true one-tenth liter flask, is of the highest interest. Hitherto, it has been necessary to keep certain flasks for sugar analysis alone, in laboratories which are otherwise equipped with volumetric apparatus graduated in accordance with the true metric system.[1]

Within a year, Belgian chemists have inaugurated a movement in the association with the view of obtaining the cooperation of the Belgian Bureau of Standards in the testing of chemical measuring instruments, and in the establishment of standards therefore. Their discussions on this subject may be found in the recent issues of the *Bulletin de L'Association Belge des Chimistes*, beginning with the number for December 1898, which con-

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[1] Wiley: This Journal, 21, 73.

tains a criticism of the regulations of the Kaiserliche Normal-Aichungs-Commission by L. L. de Koninck.

The regulations of the Kaiserliche Normal-Aichungs-Commission for the construction, graduation, and verification of chemical instruments for measuring volume, while still in a stage of evolution, have stood the test of a five years' trial and the critical examination of three international congresses of chemists who are interested in all refinements of apparatus and methods consistent with practical results. Some criticisms of the minor details of these regulations have been made. Notably, by Dr. Julius Wagner in his "Maassanalytische Studien," published by Oskar Liner, Leipzig, 1898. Dr. H. P. Talbot has very kindly consented to prepare a review of Dr. Wagner's paper for this Journal, and thus bring the criticisms contained therein before the society for consideration. The most serious mistake of the Aichungs-Commission's regulations, namely, the directions for testing the minor divisions of burettes, has been corrected in the supplemental regulations issued in 1897.

There has also been some dissatisfaction among technical chemists concerning the special hydrometer for sugar solutions as constructed and tested in accordance with the Aichungs-Commission's regulations (geaichte saccharimeter). See Weinstein, "Ueber die geaichten Saccharimeter" (*Ztschr. angew. Chem.*, (*1899*), 369–70; *Chem. Centrbl.*, (*1899*), I, 1098) and the other articles therein cited written by Göckel, Bruhns, and Classen.

The regulations, as a whole, must be regarded as a long step in advance, and, by their adoption, European chemists have placed themselves in a position to obtain with readiness and without excessive cost, instruments of a high degree of accuracy and of a desirable form of construction. It now remains for American chemists to follow their example.

THE WORK OF AMERICAN CHEMISTS.

The question of the importance of legal standards for measuring instruments has frequently been raised by American chemists, and parties to suits at law and to commercial transactions are almost every day impressed with the need of standards of this kind. The Association of Official Agricultural Chemists seems to have been the first scientific body of this country to undertake seriously the work of improving the quality of our measuring instruments.

In the writer's recommendations of "subjects appropriate for investigation during the ensuing year" at the close of his report as "Reporter on Methods of Sugar Analysis of the Association of Official Agricultural Chemists for 1895," the following words were used: "A comparison of the accuracy of the various grades of Brix spindles offered for sale by apparatus dealers. A comparison of the accuracy of the graduated glassware offered for sale by apparatus dealers, with the view of prescribing the limits of error allowable in graduated glassware to be used in official work. A similar comparison of the thermometers offered for sale by the dealers."[1] No action was taken, however, by the 1895 convention.

At the meeting of the association just named, held in 1896, a committee was appointed to consider the question of standards for volumetric apparatus, standard temperature for specific gravity determinations, etc. This committee, composed of B. W. Kilgore, C. L. Penny, and E. E. Ewell, made a preliminary report to the convention of 1897.[2] The committee was continued and its membership increased to five, G. C. Caldwell and H. W. Wiley being appointed as the additional members.

At the winter meeting of the American Chemical Society, held in Washington, 1897, the writer, acting on the suggestion of Prof. B. W. Kilgore, chairman of the committee of the Association of Official Agricultural Chemists just considered, introduced the following motion: "That a committee of five be appointed by the president to study and report upon the means by which the society can hasten the adoption of uniform systems of graduation, definite limits of accuracy, and standard methods for using all forms of measuring instruments in use in chemical laboratories. Further, that the committee be instructed to cooperate with other scientific bodies which have undertaken this work, or which may enter upon it in the future." This motion was referred to the council, and, after favorable action by that body a committee was appointed, which, after the successive resignations of Profs. Kinnicutt and Venable, is now composed of H. P. Talbot, C. E. Linebarger, G. E. Barton, Louis A. Fischer, and the writer.

The committee was promptly organized by correspondence after its members had been notified of their appointment by the secretary of the society. After much correspondence, it was agreed by a majority vote of the committee that no formal report be made at or previous to the meeting of the society held in Boston, August, 1898. In the meantime, at the suggestion of the chairman of the committee, the president of the society extended a formal invitation to the superintendent of the U. S. Coast and Geodetic Survey to present a paper at the Boston meeting of the society, in which should be described the facilities for standardizing chemical measuring instruments afforded by the U. S.

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[1] See the Proceedings of the Twelfth Annual Convention of the A. O. A. C., Bulletin No. 47, Division of Chemistry, U. S. Department of Agriculture, page 154.

[2] See Proceedings Fourteenth Annual Convention of the A. O. A. C., Bulletin No. 51, Division of Chemistry, U. S. Department of Agriculture, pages 137-139 and 159-164.

Office of Standard Weights and Measures and by similar bureaus of foreign governments.

In response to the request, a paper on this subject was presented at the Boston meeting by Mr. Louis A. Fischer, of the Office of Standard Weights and Measures. By a vote of the society, this paper was referred to the Committee on Papers and Publications, with the recommendation that it be published in the Journal, as has been announced by the secretary of the society in his report of the meeting.

At the close of his paper, Mr. Fischer recommended that the society adopt the following definitions of the liter, density, and a degree of temperature :

"1. The liter, as defined by the International Committee of Weights and Measures ; *viz.*, the volume of the *mass* of a kilogram of pure water at the temperature of maximum density, and under a pressure of 760 mm. of mercury.

"2. Density, defined as the ratio of the mass of a substance to that of an equal volume of pure water at its maximum density (4° C.).

"3. The centigrade degree of the hydrogen thermometer of the International Bureau of Weights and Measures."

Mr. Fischer also recommended "that the society adopt some convenient temperature, at which all volumetric apparatus shall contain their stated capacities."[1] These recommendations were referred to the committee for consideration.

A paper on "Volumetric Apparatus" was read at the Boston meeting by Mr. G. E. Barton, a member of this committee. In the course of his paper, which has already appeared in the Journal, Mr. Barton very clearly shows the need of standards for this class of measuring instruments.[2]

During sessions of the committee held at the time of the Boston meeting of the society, it was voted to limit the work of the committee for the present to the consideration of the proper form, system of graduation, limits of accuracy, manner of labeling, and methods of using volumetric apparatus.

The following motion, further defining the work of the committee for the immediate future, was presented by Prof. F. P. Venable, and adopted by a vote of the committee :

"That the members of the committee take under consideration the reports of the German Commission and the Vienna congress and, after making such corrections or additions as may be agreed upon, use this as a basis for a report to the society."

The writer presented to the committee a somewhat elaborate scheme for securing the cooperation of the members of the society in a study of the quality of chemical measuring instru-

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[1] This Journal, 20, 912–927 (*1898*).

[2] *Ibid.*, 20, 731–739 (*1898*).

ments now in use, with the view of increasing the interest in the work of the committee and at the same time obtaining evidence of the directions in which reforms were most greatly needed. As the plan only received the hearty approval of one other member of the committee, it was abandoned.

The committee is now striving to bring before the council at an early date a series of recommendations which include certain definitions of fundamental standards, and the request that the U. S. Office of Standard Weights and Measures adopt regulations governing the construction, calibration, verification, etc., of chemical measuring instruments, as mentioned at the opening of this paper.

As the chairman of the committee, I take this opportunity to announce that the committee will be very glad to answer inquiries or to accept suggestions from the members of the society whenever they may find it convenient to offer them. I shall be especially pleased to see discussions of the subject of standards for volumetric apparatus or for other forms of measuring instruments, presented in this Journal. ERVIN E. EWELL.

WASHINGTON, D. C., March 7, 1899.

NEW BOOKS.

MAASSANALYTISCHE STUDIEN. Habilitationsschrift. VON DR. JULIUS WAGNER. Leipzig: Oskar Leiner. 1898. pp. 123.

Since the adoption of the regulations of the Kaiserliche Normal-Aichungs-Commission of Berlin in June, 1893, those regulations have probably been generally accepted as representing the best results of mature thought upon questions relating to practical and desirable accuracy in the graduation and calibration of volumetric apparatus, and the precautions to be taken to ensure the preparation of trustworthy utensils. Committees appointed by three International Congresses have practically adopted the equivalent of these regulations as expressing their views, and only a few minor modifications were adopted by the Aichungs-Commission in 1897 In the little volume under consideration, Part I of which is devoted to general sources of error in volumetric analyses, Dr. Wagner has criticised certain of the conditions prescribed by the Normal-Aichungs-Commission as inadequate, and presents experimental data in support of his statements. This criticism demands some attention at this time, from its close connection with the work of the Committee on Measuring Instruments appointed by the President of the American Chemical Society to consider what steps should be taken, or regulations adopted, to promote uniformity of standards and practice, and greater accuracy of manufacture in connection with measuring utensils.

In the opinion of Dr. Wagner apparatus having the stamp of the Normal-Aichungs-Commission requires reexamination before it can be used in scientific investigations, because the degree of accuracy demanded is less than is attainable in the chemical processes in connection with which it is used, and also less than is practically attainable in manufacture and graduation. Dr. Wagner first refers to Classen's criticism of the regulations of the commission[1] because no account is taken of the variation in the amount of fluid which adheres to the walls of the vessels in the case of fluids of varying character. Dr. Wagner first shows that glass utensils are apparently most readily and completely cleansed by treatment with sulphuric acid and potassium bichromate, and notes the striking fact that a pipette containing a very thin layer of oil on its inner surface delivers more liquid than when thoroughly cleaned. He then studies the behavior of solutions of twentieth-normal bichromate, normal sodium carbonate, of concentrated sulphuric acid, and of several concentrated salt solutions, and determines, by weighing, the volume of the liquid adhering to the burette. His results indicate that the differences lie within the limits of error of observation, except in the case of concentrated sulphuric acid, from which it appears that the criticism of Classen is not well founded.

The first of the measuring instruments discussed is the pipette. Regarding the accuracy to be demanded in the use of pipettes, Böckmann, in his *Chemische Technische Untersuchungen, 1893*, I, 178, places the average value of the allowable error at 2/1000 for volumes from 1 to 25 cc., and 1/1000 from 50 to 2000 cc. This may be regarded as a fair statement of the requirements for technical use; yet, as is pointed out, the Aichungs-Commission's regulations allow a variation of 1/100 for a one cc. pipette; 1/200 for two cc.; 4/1000 for five cc.; 2/1000 for ten cc.; 1/1000 for twenty-five, fifty, and one hundred cc.; a lack of uniformity which may in itself become a source of error.

To indicate the degree of accuracy which might properly be

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[1] Mohr's Titrirmethode, 7th Edition, p. 55.

demanded for research work, Dr. Wagner examined fourteen pipettes, varying from 100 cc. to 10 cc. capacity, and finds that the contents of a pipette may be determined to 2/10000 of its value for pipettes larger than ten cc., and probably to 4/10000 for ten cc. and five cc. pipettes, and that the error arising from the use of a pipette need not exceed these amounts. These quantities are much less than the limits set by the Aichungs-Commission, and a regraduation of instruments tested by this commission is therefore essential for work of high accuracy.

Regarding the method of emptying a pipette, whether by allowing the liquid to run freely, and, at the expiration of a definite time, touching the tube against the side of the vessel, or by gently blowing out the last drop, the data obtained by Wagner are not conclusive, as no advantage is evident on the side of either method. The differences are within the errors of observation. Convenience seems to favor the removal of the liquid by blowing.

But the question may properly arise, whether it is practicable to graduate burettes with an exactness corresponding to that which has just been stated to be attainable in measuring their contents. This, it is stated, may be done, if the restrictions as to the internal diameter of the tubes are suitably made. The Aichungs-Commission demands, in general, that the internal diameter of the tubes shall not be less than five-tenths mm. nor more than six mm. but without further specifications. The position of the mark cannot be accurately fixed within five-tenths mm. while a greater variation is not infrequent, and pipettes are found on the market with tubes so large as to make this uncertainty in marking a source of considerable error. On the other hand, a diameter of five-tenths mm. is so small as to make the use of a pipette annoyingly tedious. A table is given showing the allowable internal diameter in order that the error in marking may not cause an error in volume exceeding 3/10000, the adoption of which would add to the concreteness of the Aichungs-Commission's regulations. In the opinion of Dr. Wagner, the requirements of the Commission that at the orifice the walls of a pipette shall be drawn out as thin as is practicable tends to produce a capillary opening, which is undesirable; this fact leads him to favor blowing out the last drops of liquid as a method of emptying the pipettes now on the market.

Dr. Wagner notes great inequality in practice as regards the time of drainage. He recommends that pipettes should be so constructed with respect to the size of the orifice, that the time of outflow shall be sufficiently long to avoid any after-drainage, rather than to empty the pipette rapidly and to wait for a definite interval. He makes certain statements as to the time necessary to accomplish this.

A similar irregularity in allowable error to that noted in the requirements regarding pipettes is found with respect to measuring flasks, and it is pointed out that, for a variation of one mm. in the position of the mark, the maximum diameter allowable in 500 cc. and 50 cc. flasks as stated by the Commission should be reduced from twenty and ten mm. to fourteen and eight mm. respectively, in order to conform to the allowable variation in cubic centimeters, as stated in the very same regulations of the Commission. Measuring flasks may apparently be read with an accuracy about five times as great as that demanded by the Commission's regulations, with respect to graduation. The author believes that the manufacturers would welcome more explicit statements regarding the allowable variations in the diameter of the necks of the flasks.

Following a discussion of the limit of error in burette readings, the author points out inconsistencies similar to those already noted in the limit of accuracy demanded for burettes by the Aichungs-Commission's regulations, and points out that by suitably limiting the diameter of the burette, uniform accuracy is attainable. Burettes containing fifty cc. should have a diameter of ten to eleven mm., those of thirty cc. eight to ten mm., ten cc. graduated pipettes, five to seven mm. Assuming a necessary minimum error of one-tenth mm. in reading the position of the meniscus, the percentage error is always less than 1/1000, if the above dimensions are adhered to.

The original statement in the Commission's regulations regarding the allowable error in the small divisions of a burette seems to have been unsatisfactory, and was revised in 1897 but in such a way that, according to Dr. Wagner, it is satisfactory with respect to accuracy, but almost impossible to execute, and he recommends that, instead of striving to attain unreasonable exactness, each burette be accompanied by a table of corrections (a request made by the Verein Deutscher Chemiker, but set aside by the Commission without assigned reason), or that the results of the calibration be written upon the burette itself.

The Commission places the time to be allowed for a burette to drain at two minutes, but the author regards it as a more advantageous and less time-consuming practice to allow the liquid to run out at the rate of ten cc. in about ten seconds, in which case the reading may be taken at once without appreciable error.

As a result of his work Dr. Wagner makes these recommendations regarding the graduation and calibration of measuring vessels: (1) That they be divided into grades, with respect to accuracy, and that the grade to which each instrument belongs be plainly marked upon it; (2) that the highest grade for pipettes and measuring flasks include only those accurate within 5/10000 of their capacity; and (3) that, since burettes cannot be graduated with an exactness corresponding to the accuracy desired for scientific work, they should be so calibrated as to assure accuracy within one-tenth mm. at any point of measurement, and that the value of each individual cubic centimeter shall be tested.

The sources of error connected with the process of weighing are next considered and, assuming, in general, an accuracy of one part in one thousand as attainable in analysis, it appears that the reduction of weighings in air to those *in vacuo* is not requisite, since the error is less than the fraction just named. Following this discussion a warning is sounded against the acceptance of reagents of "guaranteed" purity as reliable; the methods of testing reagents are also discussed, and Krauch's "*Die Prüfung der chemischen Reagentien auf Reinheit*" is severely criticised. The closing pages of this part of the volume are devoted to a consideration of the influence of temperature-changes upon the accuracy of volumetric work. It appears that, in general, decinormal solutions may be regarded as having a coefficient of expansion equal to that of water, but solutions of greater concentration require special tables of corrections; a few values for such solutions are given in this work. The author advocates the adoption of 20° C. as a standard temperature for calibration, rather than 15° C. as named in the Aichungs-Commission's regulations, considering the higher temperature to be more convenient for laboratory use.[1]

Part II of the dissertation is devoted to methods of standardization employed in iodimetry. The conclusions arrived at may be summed up as follows: (1) That the standardization of a thiosulphate solution may be made accurate to one-tenth per cent.; (2) that the best of the bichromates, iodates, and bromates found in the market are very likely to be impure; and (3) that the presence of potassium bichromate promotes the oxidation of hydriodic acid by atmospheric oxygen and by interfering with the end-point introduces a possible error when the bichromate is used for standardizing purposes.

Part III presents the results of study of the reaction between potassium permanganate and hydrochloric acid, under the influence of certain substances exerting a catalytic influence. Dr. Wagner sums up his results as follows: (1) The decomposition of permanganate in iron titrations in the presence of hydrochloric acid is the result of the intermediate formation and oxidation of a ferrohydrochloric acid; (2) other salts, such as those of chromium, cadmium, as well as gold and platinum chlorides, cause the same decomposition; (3) platinohydrochloric acid was found to be oxidized more readily than hydrochloric acid; (4) by means of cryoscopic methods the existence and gradual formation of a cadmiohydrochloric acid was indicated; (5) the presence of barium chloride with ferrous salts, causes an essential increase in the decomposition of the permanganate, amounting even to forty-five per cent.; (6) in many chemical changes secondary reactions may take place, without, however, as in the case of real catalysis, increasing the speed of the primary reaction. The secondary reactions seem then to add their effect to that of the primary reaction. Dr. Wagner proposes the term "Pseudo-Katalysen" to indicate reactions of this character.

The dissertation is marked by a somewhat aggressive spirit of criticism, but it contains much which bears evidence of careful thought and labor, and is well worth perusal.

H. P. TALBOT.

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[1] The regulations of the Normal-Aichungs-Commission have also been criticised by Professor L. L. de Koninck in an article entitled "Observations relatives aux conditions du contrôle des appareils de mesure en volume par la Commission d' étallonnage normal d'Allemagne," published in the *Bull. de l' Assoc. Belge des Chemistes, Dec., 1898.*

BOOKS RECEIVED.

Curing and Fermentation of Cigar Leaf Tobacco. By Oscar Loew. Report No. 59, U. S. Department of Agriculture (Division of Vegetable Physiology and Pathology), Washington, D. C. 34 pp.

Farming in North Carolina, being some hints as to the more profitable use of the soil and crops of the state. By W. F. Massey. Bulletin No. 162. The North Carolina Agricultural Experiment Station, Raleigh, N. C. 32 pp.

Commercial Feeding Stuffs in the Connecticut Market. Bulletin No. 128. April, 1899. 12 pp. Inspection and Care of Nursery Stock. Bulletin No. 129. May, 1899. 10 pp. Connecticut Agricultural Experiment Station, New Haven, Conn.

Twenty-second Annual Report of the Connecticut Agricultural Experiment Station for 1898. Part II.—Food Products. 121 pp. The Connecticut Agricultural Experiment Station, New Haven, Conn.

Chemistry and Metallurgy Applied to Dentistry. By Vernon J. Hall, Ph.D. Evanston, Ill.: The Technical Press. vii + 246 pp.

The John Crerar Library.—Fourth Annual Report, for the year 1898. Chicago: Printed by order of the Board of Directors. 1898. 40 pp.

Qualitative Analysis for Secondary Schools. By Cyrus W. Irish, A.B. New York: American Book Co. 100 pp.

Bulletin No. 80.—1. Some Pests Likely to be Disseminated from Nurseries. 2. The Nursery Inspection Law. 73 pp. Bulletin No. 81.—A Method of Avoiding Lettuce Rot. 2. Potato Scab Experiments. 11 pp. Kentucky Agricultural Experiment Station.

Studies on Subterranean Organs.—Compositae of the Vicinity of Manhattan, Kansas. By A. S. Hitchcock. Kinderhook Faunal Studies: 1.—Fauna of the Vermicular Sandstone of Northview, Webster Co., Mo. By Stuart Weller. The Relations of Internal Pressure, Volume, and Temperature of an Isolated Mass of Perfect Gas of Uniform Temperature and in Equilibrium under the Action of its own Forces. By Calvin M. Woodward. On Gravitation in Gaseous Nebulae. By Francis E. Nipher. Transactions of the Academy of Science of St. Louis, Vol. IX.

The Newer Remedies. A Reference Manual for Physicians, Pharmacists, and Students. By Virgil Coblentz, A.M., PhD. Third Edition. Revised and very much enlarged. Philadelphia: P. Blakiston's Son & Co. 1899. 147 pp. Price, $1.00

CORRECTION.

In the March number, 1899, page 259, line 20 from top, for "0.3081 gram and 0.2997 gram, from each," read "0.0308 gram and 0.0300 gram, average of several."

PROCEEDINGS.

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Issued with January Number, 1899.

Proceedings.

COUNCIL.

The salary of the editor for 1898 has been fixed at two hundred and fifty dollars ($250).

The number of pages in the December number of the Journal was ordered increased to not over 175.

The Committee on Life Membership Fund, appointed at the meeting of the Council, August 22, 1898, has reported as follows:

To the President and Council of the American Chemical Society:

GENTLEMEN—Your Committee on the Life Membership Fund has the honor to report that it finds that the following persons have been enrolled as life members or as life associate members.

Life Members—C. F. Chandler, W. M. Habirshaw, T. S. Hunt, W. P. Mason, E. Waller.

Life Associate Members—J. O. Donner, H. C. Havemeyer, T. A. Havemeyer, A. Kuttroff, W. Pickhardt, W. P. Prentice, C. H. Senff.

That the commutation fee for life members and life associate members is one hundred dollars, and that no money appears in the treasury to the account of any one of these persons; therefore your committee recommends that the treasurer be authorized and directed to take from the moneys in the treasury, not otherwise appropriated, twelve hundred dollars ($1,200), and invest this sum as provided for in Section 2, of Article X, of the Constitution of the American Chemical Society, as adopted December 2, 1897, and that the fund thus created be hereafter held and used as a life-membership fund as provided for in the section above cited.

Respectfully submitted,
CHARLES E. MUNROE,
CHAS. B. DUDLEY,
CHAS. F. MCKENNA.

This report was approved Dec. 12th, and the recommendations therein contained adopted by the Council.

NAMES PROPOSED FOR MEMBERSHIP.

Barnett, Edwin S., Mt. Alverno, Delaware Co., Pa.

Bossé, Karl K., 158 Waverly Place, New York City.
Bradley, Walter P., 242 High St., Middletown, Conn.
Brewster, Edward E., 316 E. C St., Iron Mountain, Mich.
Brush, Charles F., 1003 Euclid Ave., Cleveland, O.
Closson, C. D., Ohio Med. Univ., Columbus, O.
Coggeshall, George W., 13 Prescott Hall, Cambridge, Mass.
Cook, Robert A., 66 Maiden Lane, New York City.
Crane, Fred., 142 Walnut St., Montclair, N. J.
Dieckmann, Otto, 1182 Harrison Ave., Cincinnati, O.
Gallivan, Frank B., Polytechnic Institute, Brooklyn, N. Y.
Giddings, H. DeWitt, 173 Loomis St., Burlington, Vt.
Gruener, Hippolyte, Adelbert College, Cleveland, O.
Haigh, Frederic, 677 E. 24th St., Paterson, N. J.
Hardenburgh, Louis M., Iron Mountain, Mich.
Harris, Isham G., H. R. State Hospital, Poughkeepsie, N. Y.
Hesse, Bernard C., 128 Duane St., N. Y. City.
Hiltner, Martin E., 1301 N St., Lincoln, Nebr.
Kelly, Daniel J., U. S. Patent Office, Washington, D. C.
Kendall, Robert E., 96 Warren St., Glens Falls, N. Y.
Levene, Phoebus A., 1626 Madison Ave., N. Y. City.
Levison, W. Goold, Cooper Institute, N. Y. City.
Porter, Arthur F., 143 Lexington Ave., New York City.
Riddle, Robert N., Uwchland, Chester Co., Pa.
Rippetoe, J. J., Vallejo, Cal.
Sadtler, Samuel S., 235 Jefferson Ave., Brooklyn, N. Y.
Schuyler, Erwin H., Watertown High School, Watertown, N.Y.
Sovereign, Clarence L., 128 N. Winnebago St., Rockford, Ill.
Thatcher, Roscoe W., Beatrice High School, Beatrice, Nebr.
Thompson, Milton S., Box 1, Newburyport, Mass.
Von Egloffstein, Camill, 714 Bushwick Ave., Brooklyn, N.Y.
Welt, Ida, 814 Lexington Ave., New York City.
Wolff, Frank A., U. S. Coast and Geodetic Survey, Washington, D. C.

NAMES PROPOSED FOR ASSOCIATE MEMBERSHIP.

Becket, Fred. M., 310 W. 122d St., New York City.
Caldwell, John A., Jr., Cornell Univ., Ithaca, N. Y.
Duff, Wm. A., 310 W. 122d St., New York City.
Hall, Gaylord C., Box 506, Central Univ., Richmond, Ky.
Hildreth, Edward T., 87 University Road, Brookline, Mass.
Hoeppner, Josephine M., Pullman, Wash.
Kingsley, William J., 202 Broadway, N. Y. City.
Loeser, Robert M., Stanford Univ., Cal.
Lysle, Walter S., 223 Chartiers St., Allegheny, Pa.
Macdonald, N. L., Everett, Mass.
Meader, Arthur L., Norwood, Cincinnati, O.
Packer, Samuel C., 4263 Fergus St., Cincinnati, O.

Porter, John J., Station C, Cincinnati, O.
Ripley, Philip F., Andover, Mass.
Robeson, Anthony M., "The Gracemore," 120th St. and Morningside Ave., New York City.
Roller, Harry C., Cranford, N. J.

NEW MEMBERS ELECTED DECEMBER 27, 1898.

Aller, F. D., Maurer, N. J.
Bosart, Louis W., Jr., Home City, Hamilton Co., O.
Cairns, Fred. I., 246 Park Ave., Bridgeport, Conn.
Clementson, Henry, 316 Cumberland St., Brooklyn, N. Y.
Converse, William A., 29 to 33 Rialto Building, Chicago, Ill.
Duryea, Chester B., Sioux City, Iowa.
Ebersole, Morris R., Cornell University, Ithaca, N. Y.
Granja, Rafael, care of C. O. Mailloux, 150 Nassau St., N.Y. City.
Hirschmann, Morris, 1363 Prospect Ave., Brooklyn, N. Y.
Holden, Edward F., Lake Ave., Melrose, Mass.
Klein, Otto W., 280 Broadway, N. Y. City.
Means, R. F., 6 Custom House St., Boston, Mass.
Miller, Frank W., Univ. of N. C., Chapel Hill, N. C.
Ward, Delancey W., 247 Sanford Ave., Flushing, N. Y.
Wyatt, Francis, 39 South William St., N. Y. City.

ELECTED DECEMBER 30, 1898.

Meyer, Max, 157 W. 103d St., N. Y. City.

ASSOCIATES ELECTED DECEMBER 27, 1898.

Bursner, J. M., 802 Vine St., Cincinnati, O.
Faulkner, Joseph G., 2529 Chatham St., Cincinnati, O.
Fite, Campbell C., 1 Madison Ave., N. Y. City.
Hawkins, Clement C., 228 W. Seventh St., Cincinnati, O.
Masury, John W., 33 W. 71st St., N. Y. City.
Treiber, C., 372 Atlantic Ave., Boston, Mass.
White, Wm. T., Box 45, Lowell, Mass.

CHANGES OF ADDRESS.

Baker, Dicia H., 2217 8th St., Birmingham, Ala.
Bevier, Isabel, Lake Erie College, Painesville, O.
Souther, Henry, 438 Asylum St., Hartford, Conn.
Waller, Elwyn, 159 Front St., New York City.

MEETINGS OF THE SECTIONS.

WASHINGTON SECTION.

The regular meeting of the Washington Section was held on

November 10, 1898. The first paper of the evening was read by Mr. F. K. Cameron, and was entitled, "Some Boiling-point Curves for Mixtures of Miscible Liquids."

The general properties and significance of pressure-concentration, and temperature-concentration curves for pairs of perfectly miscible liquids were indicated and the research of Konowaloff, Nernst, and others briefly cited. All the possible types now known were illustrated by some as yet unpublished data from a preliminary investigation by Cameron and Thayer.

A significant fact brought out by certain of these curves, notably the one for alcohol-chloroform mixtures, is that they possess not only a maximum and minimum point, but there is a decided sag in the opposite direction at another portion of the curve. So far no such curve is known which has both a maximum and minimum point, and the possibility of such a case has been denied by some authorities. But the fact just cited shows an indubitable tendency towards such a case and indicates that by a suitable choice of the constant factor (temperature or pressure) for some pair of liquids such a curve may yet be found. The great desirability of further experimental work in this field, both for theoretical and practical reasons, was indicated.

The second paper of the evening was by Mr. F. K. Cameron, and was entitled, "A Ternary Mixture."

Given a mixture of two perfectly miscible liquids, A and B, and a third substance C, soluble in one constituent of the pair. At a definite temperature there will be a separation of the liquid mixture into its constituents, this definite temperature being dependent on the relative concentrations of the solution. By keeping C in excess of the amount soluble the problem is somewhat simplified. The results of a preliminary investigation on the curve for temperatures of separation-concentration, presence of a third substance soluble in only one constituent, were presented. Further, the third substance C was varied for certain concentrations. And finally mixtures of the substances which had been used as C were tried. The results were interesting but no causal connection could be detected. It is essential that more experimental evidence shall be in our possession before a satisfactory theory of the phenomena will be possible.

The third paper was read by Dr. T. M. Chatard, and was entitled, "Note on the Rate of Loss in Cyanide Solutions."

Dr. Chatard exhibited a sheet of curves representing the rate of loss of cyanide in solutions used for the extraction of gold in the electrolytic sluice. There is always a certain loss due to oxidation of the cyanide through agitation of the solution during the operation of the apparatus. Another loss results from the action of the ore on the solution. An electric current of about two-tenths ampere per square foot of cathode plate and of about two volts, is employed and it is desirable to know what effect such a current has upon the solutions which usually contain from 0.20 to 0.25 per cent. potassium cyanide at the start. Samples of the solution were taken at regular intervals during each run, the percentage of cyanide giving points of the curve.

When ore is treated, the curves usually show a rapid loss of cyanide during the first period of fifteen minutes, due to the action of the ore, the rate of loss then decreasing so that the final result is often a fairly regular curve. When the solution is run with neither ore nor current, the fall in strength is usually regular so that the line connecting any three consecutive points is practically straight. Using the customary current but no ore, other conditions being alike, the results indicate that the cyanide losses are lessened even though the tests are, as yet, too few for positive evidence. It may, however, be stated with confidence that the use of electricity, so important for the extraction of precious metals from ores and solutions, is not attended by any increased loss of the expensive cyanide.

The last paper was read by Dr. C. E. Munroe, and was entitled, "The Examination of Acid for Use in the Manufacture of Guncotton."

Dr. Munroe's paper contained a summary of work done by his assistants, Mr. G. W. Patterson and Mr. J. J. Tobin, and by him. The specifications for the acids given were accompanied by descriptions of the analytical methods and methods of calculation to be followed in the inspection of the acids supplied, and a comparison was made between these methods and others that have been proposed. Attention was called to the necessity of defining the substances present by the methods by which they are to be determined and reckoned, as it not infrequently happens that there are differences of opinion as to the form in which they occur and the methods for determining them, and a dispute is most easily avoided by a prior technical convention. Thus there is a difference of opinion as to the form in which a portion of the nitrogen present in these acids occurs, some regarding it as in the form of hyponitrous acid, others as nitrosulphuric acid, but without expressing any opinion on this point the specifications simply required that it should be determined in a carefully prescribed manner and reckoned as nitrogen tetroxide (N_2O_4) and that as thus determined and reckoned it should not exceed a certain percentage of the mixture.

The data of a considerable number of analyses showing the percentage composition and specific gravities of both original acids and spent acids from the guncotton manufacture was given, and the differences between the amounts of sulphuric acid in the different operations was seen to be remarkably constant, showing the mixture to be well proportioned for this purpose.

Observations were made on the permanency of composition of the mixed acids stored in darkness and in sunlight; on the color of the acids as a criterion of the amount of nitrogen oxides present; on the change of color produced by heating them; on the freezing of the acids and the rate of expansion of different mixtures.

The specific gravity bottle used, which was devised by Professor Barker, and which was particularly adapted to this work, was exhibited.

WILLIAM H. KRUG, *Secretary*.

RHODE ISLAND SECTION.

The regular monthly meeting of the Rhode Island Section of the American Chemical Society was held at the Hope Club, Providence, October 27, 1898, with Mr. Edward D. Pearce as presiding officer.

Prof. J. H. Appleton, of Brown University, presented a paper on "Some Elements Recently Announced." The speaker discussed the substances proposed during the summer of 1898 as new elements: neon, metargon, krypton, xenon, etherion, coronium, monium, and polonium. In the paper all the facts and data respecting these substances, as far as published to date, were collected.

The regular monthly meeting of the Rhode Island Section of the American Chemical Society was held at the Hope Club, Providence, December 15, 1898, at 8 o'clock, with Mr. Edward D. Pearce as presiding officer.

After dinner the members and guests proceeded to the Chemical Laboratory of Brown University. Here Professor J. H. Appleton gave a lecture on "Experimentation in Organic Chemistry." His remarks were illustrated by experiments performed with simple appliances of his own invention. These experiments showed how a number of the facts and operations of organic chemistry may be demonstrated neatly, quickly, and conclusively.

The reduction of cupric oxide by sugar and the carbon dioxide formed were easily shown. The presence of nitrogen in albumen was illustrated by two processes. Chlorine in chloroform was demonstrated by passing it through a hot tube and collecting the products of decomposition. All these experiments were performed by simple devices, easily made, and mark an improvement in qualitative work of this kind.

WALTER E. SMITH, *Secretary.*

NEW YORK SECTION.

The local section of the American Chemical Society held its regular meeting at the College of the City of New York on Friday evening, November 9, Dr. William McMurtrie presiding, and ninety-five members and visitors present. The following papers were read:

"Preliminary Note on Proposed Patent Legislation in its Relation to American Chemists," by C. C. Parsons.

"Atomic Weight as a Cyclic Function," by Thomas Bayley, England.

"Recent Progress in Photochemistry," by L. H. Friedburg.

"The Commercial Electrolysis of Salt in the United States," by H. Carmichael.

"Notes on the Electrolysis of Salt," by J. D. Pennock.

On motion the chair was authorized to appoint a committee of five to consider what action should be taken on proposed patent legislation.

The chairman reported that the Chemists' Club had been duly organized and the rooms leased, and it was expected that all necessary furnishing would be completed in time for the meeting of the general society in the holiday week.

The announcement was made that the membership of the section has passed the 300 mark, which, in accordance with the provisions of the new constitution, allows the section four representatives on the council.

The secretary was therefore directed by unanimous vote to cast a ballot electing the following gentlemen to represent the society: William McMurtrie, A. A. Breneman, C. A. Doremus, and A. H. Sabin, and in the event of any of these being elected councilors-at-large, Durand Woodman, J. B. F. Herreshoff, E. G. Love, E. E. Smith, Geo. C. Stone, and C. B. Voorhees as alternates in the order named.

The Executive Committee decided to postpone the next regular meeting of the section to Friday, January 13th, to avoid following the midwinter meeting too closely. The general secretary reported a number of papers already promised for the midwinter meeting, and all arrangements progressing favorably.

DURAND WOODMAN, *Secretary.*

CINCINNATI SECTION.

The sixty-fourth regular meeting of the Cincinnati Section was held on Thursday, December 15th, in the Chemical Lecture Room of Hanna Hall, University Buildings, with fifteen members present and President O. W. Martin in the chair.

Prof. T. H. Norton read an interesting paper on the "Occurrence of the Diamond in Various Parts of the United States, and on the First Occurrence of the Diamond in Ohio." The exhibition of various specimens of diamonds, including that found in Ohio, and the experiment demonstrating the combustibility of this substance, lent additional interest to the paper. The gem found in Ohio presented in its cut state an unusual degree of brilliancy, while measurements of its specific gravity gave a result markedly higher than with any diamond hitherto observed, which would suggest a connection between its specific gravity and its refractive properties. This point Professor Norton intends further to investigate.

Mr. Willett C. Pierson then addressed the meeting on "The Mechanical and Chemical Testing of Cement," exhibiting specimens and charts illustrative of the subject.

The election of officers of the section for 1899 was finally held, and resulted as follows:

President—Wm. Simonson.
Vice-presidents—R. M. Hughes and J. N. Hurty.
Secretary—S. Waldbott.
Treasurer—Henry B. Foote.
Directors—Thomas Evans, D. J. Ogilvy, and Wm. H. Crane.

Upon motion the meeting adjourned.

S. WALDBOTT, *Secretary.*

CHICAGO SECTION.

The November meeting of the Chicago Section was held at the Technical Club, 230 South Clark Street, Tuesday, November 8th. After the usual dinner, Mr. Woods, of New York, described a process for extracting fats from tankage by means of light-boiling naphtha. This was followed by a general discussion of the subject.

F. B. Dains then read a paper on the preparation, properties, and reactions of the isourea ethers.

At the meeting of the Chicago Section held December 23d, the following officers were elected for the coming year:

President—C. E. Linebarger.
Vice-president—W. R. Smith.
Secretary—F. B. Dains.
Treasurer—C. W. Patterson.
Executive Committee—C. E. Linebarger, F. B. Dains, and E. K. Nelson.
Member of Council—J. H. Long.

F. B. DAINS, *Secretary.*

Issued with February Number, 1899.

Proceedings.

MINUTES OF THE EIGHTEENTH GENERAL MEETING OF THE AMERICAN CHEMICAL SOCIETY, HELD IN NEW YORK CITY, DECEMBER 27 AND 28, 1898.

TUESDAY MORNING, DECEMBER 27, 1898.

The morning session met in the Assembly Hall of the Chemists' Club, 108 W. 55th St., New York City. The meeting was called to order at 10.15 A.M., by Dr. William McMurtrie who welcomed the visiting chemists to the hospitalities of the New York Section.

Hon. Randolph Guggenheimer, president of the council of the City of New York, then welcomed the chemists to the City of New York, and President Alexander S. Webb, D.D., of the College of the City of New York, extended a special welcome on behalf of New York's educational and scientific institutions. In response, President Charles E. Munroe, of the American Chemical Society, thanked the previous speakers for the cordial welcome extended to the society, and expressed the appreciation of the members of the efforts in their behalf on the part of the New York Section.

President Munroe then called the meeting of the society to order at 10.30 A.M. On motion, M. T. Bogert was elected secretary *pro tem.*, on account of the illness of Secretary Hale. President Munroe then introduced Professor Raoul Pictet, of Geneva, who expressed his pleasure at being present, and spoke in eulogy of our country and of the work of our scientific men. Dr. McMurtrie moved "that the routine business of the society be postponed until the evening session and that we now proceed to the reading and discussion of papers." Seconded and carried.

The following is a list of the papers presented at the meeting of the society :

1. A New Method for the Separation of Arsenic, Antimony, Selenium, and Tellurium from One Another and from Other Metals. Augustus E. Knorr.

2. Measurement of Turbidity in Water. W. P. Mason.

3. Antitoxin Serum for Some Animal Diseases. E. A. de Schweinitz.

4. Separation of Impurities in the Electrolytic Refining of Copper. P. de P. Ricketts.

5. The Preparation of Metallic Tellurium. Victor Lenher.

6. The Preparation of Pure Tellurium. Henry Fay.

7. The Effect of Certain Nitrogenous Materials upon the Growth of Yeast. Harris E. Sawyer.

8. The Assay of Nux Vomica. E. R. Squibb.

9. The Potato and Cassava Starch Industries in the United States. H. W. Wiley.

10. Vanillin and Coumarin: Their Separation, Identification, and Estimation in Flavoring Extracts. (In abstract.) W. H. Hess and A. B. Prescott.

11. Emetine Octoiodide, and the Extraction and Estimation of Alkaloids generally. (In abstract.) H. M. Gordin and A. B. Prescott.

12. Notes on the Estimation of Carbohydrates. F. W. Traphagen and W. M. Cobleigh.

13. The Composition and Rancidity of Butter Fat. C. A. Browne, Jr.

14. The Action of Iodine on the Fatty Amines. James F. Norris.

15. On the Constitution of Some Canadian Baryto-celestites. C. W. Volney.

16. Laboratory Notes. A. C. Langmuir.

17. New Method for the Determination of Zinc. A. C. Langmuir.

18. Note on Drown's Method of Determining Silicon. A. C. Langmuir.

19. The Determination of Arsenic in Glycerine. A. C. Langmuir.

20. Note on Certain Flame Colorations Yielded by the Chlorides and Bromides of Nickel and Cobalt. Allerton S. Cushman.

21. Conservation of Energy in the Living Organism. W. O. Atwater.

22. Claissen's Reaction as an Aid to the Determination of the Constitution of Terpene Ketones. M. C. Burt.

23. The Determination of Sulphur in Sulphites. A. Bourgougnon.

24. Sixth Annual Report of the Committee on Atomic Weights. F. W. Clarke.

25. Report of the Third International Congress of Applied Chemistry. H. W. Wiley.

26. Improved Apparatus. J. L. Sammis.

27. The Determination of Potash as Perchlorate. F. S. Shiver.

28. Use of Compressed Oxygen in Elementary Organic Analysis; and of Soda-lime in the Quantitative Determination of Carbon Dioxide. F. G. Benedict and O. F. Tower.

29. Commercial Iron Silicides, with High Percentage of Silicon. G. de Chalmot.

30. Glycollic Acid: One of the Acids of Sugar Cane. Edmund C. Shorey.

31. The Analytical Constants of American Linseed Oil. Augustus H. Gill and Augustus C. Lamb.

32. A New Method for the Preparation of Cesium. Hugo Erdmann and A. E. Menke.

33. The Absorption of Methane and Ethane by Fuming Sulphuric Acid. R. A. Worstall.

34. Notes on the Rapid Determination of Tungsten in Steel. George Auchy.

35. The Determination of Carbon Monoxide, Methane, and Hydrogen by Combustion. L. M. Dennis and C. G. Hopkins.

36. Analytical Research on Sod Oil. Erastus Hopkins, D. L. Coburn, and Edward Spiller.

37. Table of Baumé's Hydrometer—American Standard. (By title.) Sidney S. Emery.

38. The Inversion of Sugar by Salts. (By title.) L. Kahlenberg, D. J. Davis, and R. E. Fowler.

39. The Heat of Bromination Tests for Oils. Augustus H. Gill and Israel Hatch, Jr.

40. A Balance for Use in Courses in Elementary Chemistry. C. E. Linebarger.

41. Sodium Aluminate as a Means for the Removal of Lime and Suspended Matter from Water for Use in Boilers. C. F. Mabery and E. R. Baltzley.

42. Perhalides of Quinoline. P. F. Trowbridge.

43. On The Isourea Ethers and Other Derivatives of Ureas. F. B. Dains.

44. The Action of Sulphuric Acid on Thymol. James H. Stebbins.

45. The Synthesis of Selenophen. Robert E. Lyons.

46. A New Filtering Medium. George W. Sargent and John Kirk Faust.

Papers 1, 4, and 5 were then read. In connection with the reading of his paper, Dr. Lenher exhibited a four-pound ingot of pure tellurium. A verbal abstract of paper 6 was given by Dr. Norris, and then followed a most interesting discussion, participated in by Messrs. Munroe, Mabery, Norris, Lenher, Ricketts, Knorr, and others, on the separation of selenium from tellurium and the preparation of pure tellurium, including methods for redetermining the atomic weight of tellurium. Paper 3 was read by title. Paper 2 was postponed (see minutes of Wednesday afternoon session).

The meeting adjourned at 11.45, in time to take a special train upon the Elevated R. R. at 12 o'clock, at the 58th St. Station. Crossing to Jersey City by the ferry at the foot of Liberty St., the society found a special train, provided by the Jersey Central R. R., to carry them to the New Jersey Zinc Co.'s works at Newark. After an excellent luncheon, generously provided by the latter company, the chemists inspected the works, every facility being afforded them by the officials of the company. The remainder of the afternoon was spent in visiting the following places of interest, where the chemists met with a similar welcome and most courteous treatment: Balbach Smelting and Refining Co., P. Reilly Patent Leather Works, Murphy Varnish Co., Knickerbocker Cement Co., Wetherill Concentrator Co., and Benjamin Atha and Illingworth Steel Co. The special train left the New Jersey Zinc Co.'s works shortly after 5 P.M. on its return trip, over 150 chemists having taken part in the excursion.

EVENING SESSION, DECEMBER 27.

The evening session again met in the Assembly Hall of the Chemists' Club.

The meeting was called to order by President Munroe at 8.30 P.M. On motion the reading of the minutes of the last regular meeting was dispensed with.

Secretary Hale's report, which follows, was then read by the secretary *pro tem.*, and adopted:

REPORT OF THE SECRETARY.

The progress of the society continues unabated. The year 1898 has witnessed as great development along certain lines as any year in the history of the society. Radical changes have been made this year, and we may trust that in the main these changes have been marked improvements.

The constitution and by-laws recently adopted go into full effect at the beginning of 1899, and the year 1898 has marked the transition period between the old and the new.

The council has been very largely increased, and has become the governing body in all matters pertaining to the general welfare of the society. As now constituted, the council consists of the past presidents, 11 in number, 12 members elected at large, and one representative from each local section for every hundred members or fraction thereof, and in addition, the president, secretary, and editor *ex-officio*. There will be 42 councilors for the year 1899.

There has been a net gain in the membership during the past year of 259, a slightly larger increase than in any previous year in the history of the society, and nearly twice as much as the average gain since the year 1889, when the plan was formed to establish local sections and hold general meetings in different localities throughout the country. From that date the membership and influence of the society have steadily increased until the present time, when the New York Section alone has about one-half more members than were registered on the whole roll of the society nine years ago.

The society has now ten local sections, the last one having been chartered during the present year. It is known as the North Eastern Section, and has its headquarters in Boston. The New Orleans Section, which has been reported in previous years, has been dissolved by act of the council, since it has never had more than a nominal existence.

By the courtesy of the Chemists' Club, of New York City, the library of the society has been furnished with permanent quarters, and an appropriation has been made by the council sufficient to furnish ample shelving. The resignation of the former librarian was accepted at the meeting of the council in Boston, last summer, and Mr. Marston Taylor Bogert was elected librarian in his place. The librarian is perfecting arrangements by which the advantages of the library may be enjoyed by members living at a distance, under suitable conditions regarding the safe transportation and return of the books.

The Committee on Standards of Measurement, recommended at the Washington meeting last winter, has been appointed, and will probably present a report at this meeting.

The edition of the Journal has been increased from 1,500 to 1,700, and with the present rapid growth in membership, a farther increase is likely to be demanded soon. The amount of material accepted by the Committee on Papers and Publications has accumulated so as to necessitate an increase in the size of the Journal during the present month, and it may be advisable to provide for a permanent increase in size.

The list of exchanges has been very thoroughly considered and revised by a committee appointed for that purpose. A committee has been appointed to consider the question of increasing the size of the Standing Committee on Papers and Publications. The chairman of the Committee on Water Analysis suggests that the committee be discharged, inasmuch as after considerable correspondence the members are unable to agree upon a report. The Committee on Duty-Free Importations made an exhaustive report some time ago, and this report is on file in the archives of the society.

The finances of the society have been in good condition, and under the authority of the directors a permanent investment of certain funds has been made by the treasurer, as will probably appear in his report. At the Boston meeting a committee was appointed by the council to consider the question of life memberships and the fund authorized by the constitution in connection therewith. This committee has reported to the council with a recommendation which has been adopted by that body, authorizing the setting aside as a permanent "Life Membership Fund" sufficient to guarantee in perpetuity the interests of all present and past life members.

At the general meeting in Boston last summer, three additional honorary members were elected; *viz.*, Sir William Crookes, Henri Moissan, and J. H. van 't Hoff. These gentlemen have all accepted their election with expressions of profound thanks and appreciation of the same.

The membership of the society is now constituted as follows:

Honorary members	10
Members	1298
Associates	107
Total	1415

Since the presentation of the last annual report, the society has lost, by death, the following-named members:

Ferdinand von Mueller, Melbourne, Australia; S. W. McKeown, Youngstown, O.; Henry C. Coon, Alfred, N.Y.; Pedro J. Sosa, Panama, South America; Henry Trimble, Philadelphia; William Bromwell, Brooklyn, N. Y.; Thomas L. Blalock, Baltimore, Md.

Respectfully submitted,

ALBERT C. HALE,

Secretary.

The following report from the treasurer was presented and accepted:

REPORT OF THE TREASURER FROM DECEMBER 23, 1897, TO DECEMBER, 22, 1898.

REVENUE AND EXPENDITURES.

DR.

To Journal (12 Nos.)	$2,655.27
" Secretary's office	1,150.58
" Librarian's "	288.07
" Treasurer's "	101.47
" Editor's "	51.08
" " salary	250.00
" General expense	42.79
" Expenses of Washington meeting	144.17
" " Boston meeting	88.07
" Reprinting Journals	319.60
" Authors' reprints	176.89
" Review of American Chemical Research	47.75

To Local Sections:		
New York	$150.00	
Washington	158.67	
North Eastern	299.99	
Chicago	61.66	
Nebraska	10.36	
Columbus, O	11.66	
Cincinnati, O	68.23	
		$760.57
To Commissions to General Secretary		649.00
" Special investment fund		2,156.47
" Balance in bank		13.29
		$8,895.07

Cr.

By Balance on hand December 23, 1897	$822.07
" Dues collected by General Secretary	6,490.00
" Subscriptions through Chemical Publishing Co	620.77
" Advertisements through Chemical Publishing Co	649.96
" Sales of back numbers through librarian	237.99
" Interest on balances	20.41
" " special investment	35.00
" Cash returned by Lehigh Valley Section	18.87
	$8,895.07

ASSETS AND LIABILITIES.

Dr.

To Chemical Publishing Co	$63.70
" New York Local Section	28.84
" Columbus Local Section	3.84
" Rhode Island Local Section	0.59
" Balance in favor of American Chemical Society	4,012.05
	$4,109.02

Cr.

By Special investment fund	$2,132.50
" Uncollected accounts (editor)	1,270.64
" " " (secretary)	615.00
" Balances in secretary's hands	77.59
" Cash in treasurer's hands	13.29
	$4,109.02

The library of the society does not appear in the above schedule of assets because it is not yet appraised. CHAS. F. McKENNA, *Treasurer.*

The accounts of the treasurer, as set forth above, have been examined, together with the books, vouchers, and securities, and all have been found correct, E. & O. E.

A. H. SABIN,
DURAND WOODMAN,
A. P. HALLOCK,
Finance Committee.

NEW YORK, December 22, 1898.

The librarian's report was presented and accepted as follows:

REPORT OF THE LIBRARIAN.

To the Council of the American Chemical Society:

GENTLEMEN: I have the honor to report that I was elected librarian of the society on August 22, 1898, vice F. E. Dodge, resigned. The library of the society at that time was boxed up and in storage in New York City. The chief effort of the librarian has therefore been devoted to securing for the library a place where its volumes could be properly shelved and cared for, and where they should be accessible to all the membership upon demand in person or by letter. I am happy, therefore, to be able to report that the Board of Trustees of the Chemists' Club, at 108 West 55th St., New York City, have tendered to the American Chemical Society the use of their rooms as a depository for the library of the American Chemical Society, under the following general conditions:

(1) The books, pamphlets, periodicals, etc., to be shelved at the expense of the society, under the direction of the board of trustees of the club, the shelves and other library fixtures purchased by the society, to remain the property of the society.

(2) The society to assume the expense of the preservation and insurance of its library.

(3) That access to the library may be had by non-members of the club at such times as may be mutually agreed upon by the librarian of the society and the house and library committees of the club, subject to the approval of the board of trustees of the club.

In exercise of the power conferred upon it, the Library Committee of the society, consisting of the librarian, the chairman of the New York Section, and the treasurer, have agreed to the above general conditions, and the transfer of the library will begin as soon as the necessary shelving can be installed. A home is thus assured to the library of the society, where its volumes can be carefully distributed and classified. As soon as this is accomplished, the books will be carefully catalogued, and copies of this catalogue forwarded to all the members, indicating also under what conditions books can be withdrawn from the library. It is believed that then the society will appreciate the value of having such a library, that all the membership may enjoy its benefits, and that they will take pride in keeping it thoroughly up to date, which is the *sine qua non* of a scientific library.

Respectfully submitted,

MARSTON TAYLOR BOGERT,
Librarian.

The report of the Committee on Coal Analysis was presented by Dr. McMurtrie for the committee. On motion, the report was accepted and the committee continued.

The Committee on Standard Color for Water Analysis reported their failure to agree upon any standard. The report was accepted and the committee discharged.

The report of the Committee on Atomic Weights was presented as paper No. 24 (see minutes of Wednesday morning session), to be read on Wednesday.

The report of the Committee on Standards for Instruments of Measure, was presented, and, on motion, referred to the council for action.

The report of the Committee on Nomenclature and Spelling of the Journal was presented by Dr. Hart, with the recommendation that the component elements of didymium be termed praseodymium and neodymium, instead of praseodidymium, etc. The report was accepted and the recommendation referred to the council for action.

The report of the Committee on Enlarging the Committee on Papers and Publications was presented, accepted, and referred to the council for action.

Major C. C. Parsons presented a resolution calling for the appointment of a Committee on Patents and Patent Legislation. On motion, the matter was referred to the council for action.

President Munroe then announced the result of the voting for president and councilors of the society for the coming year as follows:

President—Edward W. Morley.

Councilors for Three Years—Ira Remsen, Arthur A. Noyes, Thomas M. Drown, William McMurtrie.

Councilors for Two Years—F. A. Gooch, William A. Noyes, H. L. Wells, A. A. Breneman.

Councilors for One Year—F. W. Clarke, S. P. Sadtler, C. F. Mabery, Durand Woodman.

Prof. Raoul Pictet was next introduced and delivered a most interesting lecture upon "La suppression des phénomènes chimiques a basse température," illustrating his remarks by experiments and the lantern. He showed that hydrochloric acid, which has been cooled down by a mixture of solid carbon dioxide and ether, has no action whatever upon metallic sodium; and he also traced the relation existing between the forces controlling the atoms from astronomical, physical, and chemical points of view.

Professor Pictet was followed by President Munroe, who chose as the subject of his address, " Explosions Caused by Commonly Occurring Substances." President Munroe dwelt especially upon the recent explosion in the National Capitol at Washington, and exhibited a large number of interesting lantern slides and plans in explanation of the same.

The meeting adjourned at 11.25 P.M.

WEDNESDAY MORNING, DECEMBER 28.

The Wednesday morning session met in Havemeyer Hall of Columbia University, New York City.

The meeting was called to order by President Munroe at 10.30 A.M. President Seth Low, of Columbia University, welcomed the visiting chemists to Columbia, and Chas. F. Chandler, professor of chemistry, welcomed them to Havemeyer Hall, the chemical building of the university. Professor Chandler, in the course of his address, sketched the development of chemistry at Columbia, from the founding of the School of Mines to the present time.

The reading of papers was then taken up. Papers 7, 10, and 11, were read by title, and Dr. Wiley presented a short verbal abstract of his paper (No. 9). Paper 12 was read, and in the discussion which followed, Dr. Wiley stated that the determination of starch was still among the most difficult in analytical chemistry, the trouble being that most starches were not simple substances but usually mixtures, the character of the mixture varying according to the source from which the starch was obtained. Further, the separation of starch is by no means an easy task; ferments do not attack all starches at the same rate, nor does inversion proceed at the same rate with all starches. The chemistry of starch is still very little understood.

Papers 14 and 15 were read by their respective authors; paper 13 by title. Papers 16, 17, 18, and 19, were read by Dr. Langmuir. Paper 8 was read by Dr. Squibb. Papers 21 and 23 were read by title. Paper 24 was presented by Professor

Clarke, and Dr. McMurtrie moved "that a committee of five members of the society be appointed to confer with similar committees of other chemical societies of the world, with the object of securing uniformity in conclusions regarding atomic weights." The motion was carried. The president appointed, as such International Committee on Atomic Weights, the following members; F. W. Clarke, *Chairman*, E. W. Morley, Edgar F. Smith, J. W. Mallet, and T. W. Richards.

On motion of Dr. Wiley, the society extended a hearty vote of thanks to the following: Chemists' Club, New York Section, Columbia University, Seth Low, C. F. Chandler, Raoul Pictet, President Munroe, Messrs. Guggenheimer and Webb, N. J. Central R. R., N. J. Zinc Co., Messrs. McMurtrie, Doremus, Tripler, the Press, College of the City of New York, *Brooklyn Daily Eagle*.

Dr. Whitney moved "that all remaining papers be read by abstract." The motion was lost.

On motion, all who had brought apparatus to illustrate their papers were invited to place the same on exhibition upon the lecture table.

The meeting adjourned at 1.10 P.M., to the Industrial Laboratory of Havemeyer Hall, where a lunch was provided by the New York Section.

WEDNESDAY AFTERNOON, DECEMBER 28.

The concluding session was held in Havemeyer Hall, of Columbia University.

The meeting was called to order by President Munroe at 2.34 P.M., when the reading of papers was resumed. Papers 2, 20, and 22 were read by their respective authors. Paper 25 and all the remainder on the programme, were read by title, none of the authors being present. Dr. Hart read a communication from Prof. Norton concerning diamonds found recently in the vicinity of Cincinnati, Ohio.

The meeting then adjourned, *sine die*, at 3.25 P.M.

At 5 o'clock in the afternoon the members were welcomed to the College of the City of New York, by Professor R. O. Doremus, and were entertained by a lecture and demonstration of the properties of liquid air by Charles E. Tripler, which was very largely attended.

In the evening a complimentary dinner was given to the visiting members by the New York Section, at the Waldorf-Astoria. About 150 chemists were present. The toasts and speakers were as follows: "The Past Year," Dr. C. E. Munroe; "The Coming Year," Dr. E. W. Morley; "Our Higher Education," Dr. Seth Low; "Our Allied Science," Mr. Gano S. Dunn; "Our Guests," Dr. H. W. Wiley; "Our Friends across the Sea," Prof. Raoul Pictet; "Our Past Presidents," Dr. C. F. Chandler; "Our Science Applied," Mr. W. H. Nichols; "Our Science Taught," Prof. J. H. Appleton; "Our Absent Friends," Dr. W. P. Mason.

M. T. BOGERT, Sec'y *pro tem.*

BOARD OF DIRECTORS.

The board of directors of the American Chemical Society met on Wednesday, December 28, 1898, at the Chemists' Club. The meeting was called to order by President Munroe, at 1.23 A.M., the following directors being present: Munroe, Doremus, McMurtrie, and Chandler. M. T. Bogert was appointed secretary *pro tem.*

It was moved "that all expenditures since the Boston meeting, up to and including the present meeting, be and are hereby authorized." The motion was carried.

The meeting adjourned at 1.25 A.M.

M. T. BOGERT, Sec'y *pro tem.*

COUNCIL.

The council of the American Chemical Society met on Tuesday, December 27, 1898, at the Chemists' Club. The meeting was called to order by President Munroe at 11.35 P.M., the following councilors being present: Wiley, Doremus, Austen, McKenna, Hart, Mabery, McMurtrie, Chandler, Breneman, Clarke, and Bogert. On account of the illness of Secretary Hale, M. T. Bogert was appointed secretary *pro tem.*

Dr. McMurtrie gave notice of some proposed amendments to the constitution of the society, which had received the signatures of the requisite five members of the council, and asked for the appointment of a committee to consider the same and report thereon to the council within three months from date. The president appointed, as such committee, Messrs. McMurtrie, Breneman, and Wiley.

On motion, the secretary was directed to take the usual mode of procedure in the matter of selecting the various officers and committees to be chosen by the council for the year 1899. Dr. Wiley was appointed by the council to move the thanks of the society to the New York Section, etc., at the closing session of the meeting.

The following motions were duly made, seconded, and carried:

(1) That all nominations to membership up to the close of the present meeting, shall be considered passed upon favorably by the council whenever they shall be favorably reported by the committee and published in the Journal.

(2) That the secretary be and is hereby authorized to expend an amount not exceeding $100.00 for typewriter or other material to save time and labor in his official work.

(3) That the council hereby suggests and recommends that hereafter the customary dinner at the general meetings of the society be a subscription dinner, and not a complimentary one at the expense of the local section.

(4) That, hereafter, the editor be allowed to retain ten copies of each number of the Journal when published for editorial use.

(5) That the Eighteenth General Meeting of the society shall close on Wednesday, December 28, 1898, and shall not continue on Thursday, December 29, 1898, as suggested.

(6) That, beginning with the February number, the edition of the Journal of the society shall be increased from 1,700 copies to 2,000 copies.

(7) That the Committee on Papers and Publications be authorized to increase the size of the Journal to 125 pages, for the next three numbers.

(8) That a committee be appointed to adjust the matter of foreign postage with the editor, said committee to report to the council, and then to the board of directors; McMurtrie, C. B. Dudley, and McKenna were appointed as such committee.

Dr. Hart read letters from Drs. Trevor and Norton, relating to the publication of papers on physical chemistry in the *Journal of Physical Chemistry*. On motion, it was resolved "that, whereas the American Chemical Society now has a Journal in which similar articles can be published, the council deem it inexpedient to adopt, as its official organ, any other publication."

The following was received from Major C. C. Parsons:

"Whereas, a special committee appointed by the president is now considering changes in the Patent Law—and, whereas, a number of bills are now pending in Congress, many of which are hostile to the interests of chemical industries, Resolved that this committee be authorized to request the Congressional Committee to defer action for the present, and it is recommended by this committee that a permanent committee be appointed by the American Chemical Society on patent and related legislation."

The council thereupon voted "that a Committee on Patent and Related Legislation, to consist of twenty-five members of the society, be appointed by the president of the society, President Chas. E. Munroe to be the chairman of said committee."

The recommendation of the Committee on Nomenclature and Spelling of the Journal in regard to the words praseodymium and neodymium was adopted (see minutes of the society for the Tuesday evening session). It was moved "that the chairman appoint a committee of not less than five members of the society, to attend the Pure Food Congress in Washington, D. C., January 18, 1899, as the delegates of the American Chemical Society." The motion was seconded and carried. Munroe, McMurtrie, Little, of Boston, Appleton, of Providence, and Simon, of Baltimore, were appointed as such committee.

Dr. McMurtrie moved the thanks of the council to Dr. Munroe for his able and successful administration of the business of the society. The motion was carried unanimously.

The meeting adjourned at 1.20 A.M.

The council of the American Chemical Society met on Wednesday, December 28, 1898, at Columbia University. The meeting was called to order by President Munroe, at 3.30 P.M., the following councilors being present: Hart, McMurtrie, Wells, Noyes, Chandler, Clarke, Barker, and Bogert.

It was moved "that the Committee on Papers and Publications be and are hereby authorized to publish a portrait of the retiring president of the society in the same number of the Journal in which the presidential address is published." The motion was carried.

Dr. Noyes reported for the Committee on enlarging the standing Committee on Papers and Publications.

The report of the committee was accepted and numbers 1, 3, 4, 5, and 6 were adopted as follows:

1. That the Committee on Papers and Publications shall consist of eleven members so chosen as to include, in addition to the editor, representatives of each of the more important divisions of chemistry.

3. That no specific divisions of the subject be announced in the publication of the committee.

4. That after the committee shall have been reorganized, each and every paper submitted for publication by the society, shall be referred by the editor to that member of the committee to whose department the paper in question belongs, who shall, jointly with the editor, decide finally in regard to its publication; provided, that in case of disagreement between the editor and said member, the paper shall be submitted to the president of the society for his decision.

5. That in all matters other than the acceptance of papers for publication, the committee shall act as a whole, the editor acting as chairman and secretary.

6. That the reorganized committee shall take office on January 1, 1899, or as soon thereafter as is possible.

Recommendation No. 2 was not adopted, but it was decided to submit it to the whole (new) council by correspondence, asking first for additional nominations from the councilors, and then, after these are received, submitting the matter to ballot, directing each councilor to vote for *one name* under each division of chemistry.

M. T. BOGERT, *Secretary pro tem.*

COUNCIL OF THE AMERICAN CHEMICAL SOCIETY, JAN. 1, 1899.

Members ex-officio.

Edward W. Morley, president,	**Adelbert College, Cleveland, O.**
Albert C. Hale, secretary,	**551 Putnam Ave., Brooklyn, N. Y.**
Edward Hart, editor,	**Easton, Pa.**

The Past Presidents.

Dr. S. W. Johnson,	54 Trumbull St., New Haven, Conn.
Charles F. Chandler,	Columbia University, N. Y. City.
J. W. Mallet,	Univ. of Virginia, Charlottesville, Va.
Albert B. Prescott,	Univ. of Michigan, Ann Arbor, Mich.
C. A. Goessmann,	Amherst, Mass.
George F. Barker,	3909 Locust St., Philadelphia, Pa.
G. C. Caldwell,	Cornell University, Ithaca, N. Y.
H. W. Wiley,	U. S. Dept. of Agriculture, Washington.
Edgar F. Smith,	Univ. of Pennsylvania, Philadelphia, Pa.
Charles B. Dudley,	Drawer 334, Altoona, Pa.
Charles E. Munroe,	Columbian University, Washington, D. C.

By Special Article of New Constitution, until December, 1899.

Peter T. Austen,	346 Broadway, N. Y. City.

Councilors at Large. Term expires December, 1899.

F. W. Clarke,	U. S. Geological Survey, Washington, D.C.
Charles F. Mabery,	Case School of Applied Science, Cleveland, O
Samuel P. Sadtler,	1042 Drexel Building, Philadelphia, Pa.
Durand Woodman,	127 Pearl St., N. Y. City.

Term expires December, 1900.

A. A. Breneman,	97 Water St., N. Y. City.
F. A. Gooch,	Yale University, New Haven, Conn.
William A. Noyes,	Rose Poly. Inst., Terre Haute, Ind.
Horace L. Wells,	57 Trumbull St., New Haven, Conn.

Term expires December, 1901.

Thomas M. Drown,	Lehigh University, So. Bethlehem, Pa.
William McMurtrie,	101 W. 81st St., N. Y. City.
Arthur A. Noyes,	Mass. Inst. Technology, Boston, Mass.
Ira Remsen,	Johns Hopkins University, Baltimore, Md.

Councilors from Local Sections. Rhode Island Section.

Charles A. Catlin,	133 Hope St., Providence, R. I.

Cincinnati Section.

Alfred Springer,	P. O. Box 621, Cincinnati, O.

New York Section.

Charles A. Doremus,	17 Lexington Ave., N. Y. City.
J. B. F. Herreshoff,	19 Pierrepont St., Brooklyn, N. Y.
E. G. Love,	80 E. 55th St., N. Y. City.
A. H. Sabin,	Box 85, Long Island City, N. Y.

Washington Section.

W. F. Hillebrand,	U. S. Geological Survey, Washington, D. C.

Lehigh Valley Section.

Porter W. Shimer,	Easton, Pa.

Chicago Section.

John H. Long,	2421 Dearborn St., Chicago, Ill.

Nebraska Section.

H. H. Nicholson,	Univ. of Nebraska, Lincoln, Nebraska.

North Carolina Section.

Charles Baskerville,	**Chapel Hill, N. C.**

Columbus Section.

N. W. Lord,	**Ohio State University, Columbus, O.**

North Eastern Section.

John Alden,	**Lawrence, Mass.**
A. D. Little,	**7 Exchange Place, Boston, Mass.**
Henry P. Talbot,	**Mass. Inst. Technology, Boston, Mass.**

NAMES PROPOSED FOR MEMBERSHIP.

Banghart, Edgar D., Wymore, Nebraska.
Baxter, Wm. T., 47 St. Felix St., Brooklyn, N. Y.
Bradbury, Dr. Robert H., Central Manual Training School, Philadelphia.
Hamilton, H. C., 637 Baker St., Detroit, Mich.
Hazard, F. R., Solvay Process Co., Syracuse, N. Y.
Hoffman, John W., State A. and M. College, Orangeburg, S.C.
Horton, E. G., Lab. State Board of Health, Columbus, O.
Koch, Charles F., 2334 Ashland Ave., Cincinnati, O.
Lamar, Wm. R., 55 W. 127th St., N. Y. City.
Lamborn, Leebert L., care of Curtis Davis & Co., 136 State St., Boston, Mass.
Lee, Waldemar, 2802 W. Lehigh Ave., Philadelphia.
Linton, J. H., 3012 Wabash Ave., Chicago, Ill.
McCay, Leroy W., Princeton, N. J.
Neiman, Howard S., 8 E. 97th St., N. Y. City.
Rogers, Allen, Univ. of Maine, Orono, Me.
Schober, W. B., Lehigh Univ., South Bethlehem, Pa.
Spieler, Augustus J., care of The Will and Baumer Co., Syracuse, N. Y.
Street, John Phillips, New Brunswick, N. J.
Wagner, Dr. Theodore B., care of Glucose Sugar Ref. Co., Beach & Taylor Sts., Chicago, Ill.
Wiener, William, 62½ Nelson Place, Newark, N. J.
Wilkens, H. A. J., care of N. J. Zinc Co., 52 Wall St., N. Y. City.
Witherspoon, Thomas A., 27 Iowa Circle, Washington, D.C.

NAMES PROPOSED FOR ASSOCIATE MEMBERSHIP.

Cayvan, Llewellyn L., 660 Sixth St., South Boston, Mass.
Driehaus, Irwin W., Madisonville, O.
Fetsch, William, 2530 W. 6th St., Cincinnati, O.
Russell, George F., care of Russell Paper Co., Lawrence, Mass.
Young, Charlotte S., Mt. Hope Road, Price Hill, Cincinnati, O.

NEW MEMBERS ELECTED JANUARY 23, 1899.

Barnett, Edwin S., Mt. Alvern, Delaware Co., Pa.
Bassé, Karl Kurt, 158 Waverly Place, N. Y. City.

Bradley, Walter Parke, 242 High St., Middletown, Conn.
Brush, Charles F., 1003 Euclid Ave., Cleveland, O.
Closson, C. D., Ohio Med. Univ., Columbus, O.
Coggeshall, George W., 13 Prescott Hall, Cambridge, Mass.
Cook, Robert A., 66 Maiden Lane, N. Y. City.
Crane, Fred., 142 Walnut St., Montclair, N. J.
Dieckmann, Otto, 1182 Harrison Ave., Cincinnati, O.
Gallivan, Frank B., Polytechnic Institute, Brooklyn, N. Y.
Giddings, H. DeWitt, 173 Loomis St., Burlington, Vt.
Gruener, Hippolyte, Adelbert College, Cleveland, O.
Haigh, Frederic, 677 E. 24th St., Paterson, N. J.
Harris, Isham G., M.D., State Hospital, Poughkeepsie, N. Y.
Hesse, Bernard Conrad, 128 Duane St., N. Y. City.
Hiltner, Martin E., 1301 N. St., Lincoln, Nebr.
Kelly, Daniel J., M.D., U. S. Patent Office, Washington, D. C.
Levene, Phoebus A., 1626 Madison Ave., N. Y. City.
Levison, W. Goold, Cooper Institute, N. Y. City.
Riddle, Robert N., Uwchland, Chester Co., Pa.
Sadtler, Samuel S., 235 Jefferson Ave., Brooklyn, N. Y.
Schuyler, Erwin H., Watertown High School, Watertown, N.Y.
Sovereign, Clarence L., 128 N. Winnebago St., Rockford, Ill.
Thatcher, Roscoe W., Beatrice High School, Beatrice, Nebr.
Thompson, Milton S., P. O. Box 1, Newburyport, Mass.
von Egloffstein, Camill, 714 Bushwick Ave., Brooklyn, N. Y.
Welt, Ida, Ph.D., 314 Lexington Ave., N. Y. City.
Wolff, Frank A., U. S. Coast and Geodetic Survey, Washington, D. C.

ASSOCIATES ELECTED JANUARY 23, 1899.

Becket, Frederick M., 310 W. 122nd St., N. Y. City.
Caldwell, John A., Jr., Cornell University, Ithaca, N. Y.
Duff, William A., 310 W. 122nd St., N. Y. City.
Hall, Gaylord C., P.O. Box 506, Central Univ., Richmond, Ky.
Hoeppner, Josephine M., Pullman, Wash.
Kinsley, William J., 202 Broadway, N. Y. City.
Loeser, Robert M., Stanford University, Cal.
Lysle, Walter S., 223 Chartiers St., Allegheny, Pa.
Macdonald, N. M., Everett, Mass.
Meader, Arthur L., Norwood, Cincinnati, O.
Parker, Samuel C., 4263 Fergus St., Cincinnati, O.
Porter, John J., Station C, Cincinnati, O.
Robeson, Anthony N., The Gracemore, 120th St. and Morningside Ave., N. Y. City.
Roller, Henry C., Cranford, N. J.

CHANGES OF ADDRESS.

Lindauer, Arthur M., 302 N. State St., Ann Arbor, Mich.
Passolt, H. A., LaSalle, Ill.

Persons, A. A., University, Ala.
Pickel, J. M., West Raleigh, N. C.
Root, William L., 11 Church St., Pittsfield, Mass.

MEETINGS OF THE SECTIONS.

CINCINNATI SECTION.

The sixty-fifth regular meeting of the Cincinnati Section took place on Monday, January 16th, in the Chemical Lecture Room of Hanna Hall, University Buildings, with twenty-three members in attendance and about fifty persons present in all, President Wm. Simonson in the chair.

Dr. Wm. Groff, upon request, entertained the meeting by relating his observations on the zodiacal light in the Egyptian desert, and its bearing upon the religious rites of the Mahomedans in that region.

Prof. J. Warren Ritchey then gave an interesting account of the construction of a reflecting telescope, five feet in diameter, now being built at the Yerkes observatory in Wisconsin, and particularly designed for the purposes of photographic and spectroscopic work. The reading of the paper was well illustrated by diagrams and concluded with an exhibition of a number of rare lantern slide views, furnished through the courtesy of the speaker's brother, Mr. Willis Ritchey, the optician in charge at the Yerkes observatory, who has devised the special features of the telescope under consideration.

S. WALDBOTT, *Secretary*.

LEHIGH VALLEY SECTION.

A regular meeting of the Lehigh Valley Section was held in the Chemical Laboratory of Lafayette College, at Easton, on Thursday evening, January 19th, Dr. Joseph W. Richards presiding.

The annual report of the treasurer was read and approved.

Mr. Porter W. Shimer read a paper on "Silica and the Insoluble Residue in Cement." He compared the hydrochloric acid method with the fusion method for determining silica, and showed that, while in a great many instances the results obtained did not vary more than two-tenths per cent., he had analyzed several cements in which the hydrochloric acid method, the method commonly employed by cement chemists, gave results much too high. Four recent samples showed a difference in the percentage of silica obtained by the two methods of 2.48 per cent., 2.46 per cent., 1.1 per cent., and 1.0 per cent., respectively, in each case the silica obtained by the direct acid treatment being high. A subsequent complete analysis of the filtrate from the high silica of the first sample gave correspondingly low results for the other determinations, the alumina being low by 1.24 per cent., iron oxide by 0.64 per cent., lime by 0.28 per cent., magnesia by 0.12 per cent., and sulphuric anhydride by 0.14 per cent., a total low percentage of 2.42.

In another sample he obtained 26.9 per cent. silica by the fusion method, and 31.45 per cent. by the acid method, showing the extraordinary difference of 4.55 per cent. The physical tests of the cements showing these high differences indicated marked inferiority.

The paper was discussed by Messrs. Buck, Hart, Louder, and others.

Dr. Joseph W. Richards presented papers on " A Portable Specific Gravity Apparatus," and on "A New Form of Button Scale for Use in Quantitative Blowpipe Analysis." Dr. Richards traced the development of each apparatus from its earliest form and exhibited the latest products of his researches. The new specific gravity apparatus has an accuracy of 0.1 to 0.2, is of a convenient form for transportation, and can be used also as a hydrometer for liquids a little lighter or a little heavier than water. The button scale which Dr. Richards had made in accordance with his latest ideas is far in advance of the older forms in point of accuracy, and has a distinct advantage in the very small liability to get out of order.

The papers were discussed by Messrs. Shimer, Ullman and Hart.

Mr. Richard K. Meade exhibited an ingenious form of apparatus for the violent agitation of solutions during the passage of hydrogen sulphide or other gases.

On motion, the meeting adjourned.

BERNARD ENRIGHT, *Secretary.*

NOTICE.

Hereafter the regular monthly meetings of the New York Section will be held in the Assembly Hall of the Chemists' Club, 108 W. 55th Street, and the dates will be March 10, April 7, May 5, and June 9. All chemists are invited to attend.

Issued with March Number, 1899.

Proceedings.

COUNCIL.

The following Committee on Patent and Related Legislation has been appointed, in accordance with the vote of the Council at the New York Meeting:

Charles E. Munroe, Washington, D. C., *Chairman.*
C. Chauncey Parsons, Brooklyn, N. Y., *Secretary.*
William McMurtrie, N. Y. City.
Durand Woodman, N. Y. City.
W. H. Nichols, N. Y. City.
T. B. Stearns, Jersey City, N. J.
E. G. Love, N. Y. City.
A. D. Little, Boston, Mass.
S. P. Sharples, Boston, Mass.
S. P. Sadtler, Philadelphia.
A. M. Todd, Kalamazoo, Mich.
Henry Carmichael, Boston, Mass.
William Hoskins, Chicago, Ill.
W. B. Rising, Berkeley, Cal.
E. D. Pearce, Providence, R. I.
Joseph W. Richards, Bethlehem, Pa.
J. T. McGill, Nashville, Tenn.
N. P. Hill, Denver, Colo.
H. B. Hodges, Long Island City, N. Y.
William P. Mason, Troy, N. Y.
L. P. Kinnicutt, Worcester, Mass.
S. A. Lattimore, Rochester, N. Y.
C. H. Herty, Athens, Ga.
J. L. Fuelling, Chicago, Ill.
Isaac Adams, Annisquam, Mass.

NAMES PROPOSED FOR MEMBERSHIP.

Alway, F. J., Wesleyan Univ., University Place, Nebr.
Atkinson, J. W., Santa Maria, Cal.
Bigelow, Henry W., care of Pope Mfg. Co., Hartford, Conn.
Bigelow, Samuel L., Univ. of Mich., Ann Arbor, Mich.
Curtis, Marvin, 123 California St., San Francisco, Cal.
Divine, Robert E., 75 Niagara St., Buffalo, N. Y.

Goldstein, Harris, 15 Montgomery St., Manhattan, N.Y. City.
Greenberg, Benjamin C., 67 E. 3d St., N. Y. City.
Gross, Abraham, Duquesne Chem. Lab., Duquesne, Pa.
Hartzell, Harry S., 22 N. 8th St., Allentown, Pa.
Haskins, Henri D., Amherst, Mass.
Haywood, W. G., State Chemist's Office, Raleigh, N. C.
Hess, William H., 721 E. Huron St., Ann Arbor, Mich.
Kelly, F. G., State Chemist's Office, Raleigh, N. C.
Kumler, Albert A., Odd Fellows' Temple, 7th and Elm Sts., Cincinnati, Ohio.
Priest, George W., Watertown, Mass.
Ragland, Chas. D., Ashland, Va.
Shaw, H. I., Gilt Edge, Mont.
Snyder, Oscar J., Room 23, Y. M. C. A. Building, Minneapolis, Minn.
Stephens, W. B., Care Stephens & Bro., Marshall Ave., Cincinnati, O.
Turnbull, Davis F., 34 India St., Boston, Mass.
Tutwiler, Carrington C., 14 Bank St., Philadelphia, Pa.
Van Dyck, Edwin M., 4 Iowa Circle, Washington, D. C.
Wiechmann, F. G., 771 West End Ave., Manhattan, New York City.

NAMES PROPOSED FOR ASSOCIATE MEMBERSHIP.

Bates, Hugh H., 502 E. 3d St., Cincinnati, O.
Edgar, Wm. H., 29 Rialto Bldg., Chicago, Ill.
Fry, Harry S., Pleasant Ridge, Cincinnati, O.
Keiser, Miss Marshall, Hotel Avenel, Fort Thomas, Ky.
Kendall, Arthur I., 338 Broadway, Somerville, Mass.

CHANGES OF ADDRESS.

Barlow, W. H., Pasadena, Cal.
Brackett, E. R., 47 Jackson St., Lawrence, Mass.
Busby, Fred. E., Adams, Mass.
Cambier, Jacob, 910 Spruce St., Pueblo, Colo.
Cook, A. D., State Agr. Expt. Sta., Geneva, N. Y.
Crumbie, W. D., 146 Washington St., E. Orange, N. J.
Dortch, Fred W., Scott, Ark.
Doscher, Henry, 122 E. 37th St., N. Y. City.
Fuller, Geo. W., Court and Martin Sts., Cincinnati, Ohio.
Hayes-Campbell, J., Care Amer. Pipe & Foundry Co., Bessemer, Ala.
Johnson, Geo. A., Court and Martin Sts., Cincinnati, Ohio.
Lippincott, Warren B., Care C. K. C. S. & R. Co., Argentine, Kan.
Pickel, J. M., West Raleigh, N. C.

Pope, C. W., Room 14, 220 Devonshire St., Boston, Mass.
Starke, F. W., 1853 N. 28th St., Philadelphia, Pa.
Stebbins, J. H., Jr., 80 Madison Ave., N. Y. City.
Trubek, M., 26 E. 104th St., N. Y. City.
Wallenstein, Florian, Oranienburgerstrasse 28, Berlin N, Germany.
Waller, Elwyn, 159 Front St., N. Y. City.

MEETINGS OF THE SECTIONS.

CHICAGO SECTION.

The January meeting of the Chicago Section was held at the Technical Club, Thursday, the 26th. After the usual dinner, Professor Felix Lengfeld, of the University of Chicago, presented a very interesting paper on "Some Recent Problems of Inorganic Chemistry." He gave a sketch of recent investigations along, and opportunities for research in, such lines as the new elements, carbides, nitrides and other derivatives of nitrogen, hydrides, the nature of oxidation, alloys, the precipitation of metals by metals, etc.

Dr. J. H. Long followed with an account of the winter meeting of the American Chemical Society in New York.

F. B. DAINS, *Secretary*.

WASHINGTON SECTION.

The regular meeting of the Washington Section was held on January 12, 1899.

The first paper of the evening was read by Dr. E. A. deSchweinitz, and was entitled "The Serum Treatment of Some Animal Diseases."

In this paper the author gave a general review of the work begun in 1890 in the study of the substances secreted by the hog cholera and the swine plague germ in relation to immunity. He further pointed out the production of an enzyme by the hog cholera and other allied germs, and their importance in producing, in animals, immunity to disease. From this point the work was extended to a study of the serum obtained from animals that had been immunized to disease, and this was found to contain an immunizing principle and exerted curative properties upon experimental animals affected with hog cholera and swine plague, respectively. Following these experiments, practical work has been carried out in the field for several years, with very satisfactory results. The treatment with serum was found to save about eighty per cent. of infected herds, while in those herds not treated which served as checks the loss from disease was over eighty per cent.

In practical work in the field it is difficult to decide often, whether the animals are suffering from either hog cholera or swine plague alone, or both of these diseases. To overcome this difficulty it has appeared advisable to use a curative serum for one of these diseases mixed with a curative serum for the other. For protective vaccination it appears advisable to use in addition to the serum, the products of the bacteria as well as their cell contents, including the products of the secretion or excretion.

The second paper of the evening was read by Dr. F. K. Cameron, and was entitled, "On the Estimation of Nicotine," by E. A. de Schweinitz, J. A. Emory, and F. K. Cameron.

This paper described a critical examination of the analytical methods so far proposed, and with special reference to the so-called "Kissling method." Attempts to devise a satisfactory method were made, by the formation of double salts with metallic compounds; precipitation of an addition compound with bromine or iodine; precipitation with picric acid; precipitation with phosphomolybdic or phosphotungstic acid; decomposition of accompanying amines by nitrous acid; decomposition of these compounds with hypochlorous or hypobromous acid; separation of the ammonia as oxalate by addition of alcohol. The results were summed up as follows:

I. The so-called "Kissling method" was to be regarded as the best so far proposed. For the estimation of nicotine in tobacco leaves or powders it may be regarded as satisfactory, but its application to tobacco extracts yields very unreliable results.

II. A complete extraction of nicotine by ether and some other solvents is readily accomplished.

III. An evaporation of an ether extract will afford a practicable separation from ammonia alone, but not from other organic bases.

IV. A complete separation by distillation with steam, is much more difficult than is usually supposed. Certain deviations from the usual practice were suggested.

V. No method involving the precipitation of the nicotine in an insoluble compound has been found practicable.

VI. No method involving the decomposition of accompanying compounds has been found practicable.

VII. The presence of tertiary amines, and probably some pyridine derivatives in tobacco extracts, is as yet an insurmountable obstacle in the separation or estimation of nicotine.

Finally it is to be observed that nicotine does not yield a nitroso-compound. It comports itself as a tertiary amine. Its separation from ammonia, primary and secondary amines, can be more or less readily accomplished by the adaptation of well-known general methods. Its separation from tertiary bases must be dependent on the discovery of some accidental physical or chemical property of the substances involved, which cannot be predicated from known general principles. It would seem that a satisfactory solution of the problem is dependent on some possible empirical relation, and it is in this direction that further investigation is indicated; but it is to be hoped that a more profound study of nicotine itself will yield satisfactory evidence as to its true nature, and from the knowledge thus gained, the problem before the analyst may not be so aimless or complicated as it now seems.

WILLIAM H. KRUG, *Secretary*.

NEW YORK SECTION.

The January meeting of the New York Section of the American Chemical Society was held on Friday evening, the 13th, in the Assembly Hall of the Chemists' Club, 108 West 55th street, Dr. William McMurtrie presiding.

An arrangement for holding the meetings of the society regularly in the club building was announced and ratified by unanimous vote. Reports were made showing that the funds contributed for the expenses of the midwinter meeting had been sufficient; that the library had been moved to the club-rooms, where it was undergoing classification and arrangement, and that the resident membership had reached 100, and the non-resident nearly, if not quite, as many more.

The following papers were read: "Determination of the Bromine Absorption of Fats," by P. C. McIlhiney; "Indicators," by John Waddell; "Exhibition of Apparatus for Washing Precipitates, etc.," by W. D. Horne.

Mr. McIlhiney recommends the bromine number instead of the iodine number for identifying oils and fats, on account of the greater rapidity of reaction, greater stability of the bromine-carbon-tetrachloride solution, both before and during use, and the want of differentiation by iodine between addition and substitution compounds in the reaction.

Mr. Waddell showed some very pretty experiments, illustrating the behavior of indicators, and explanatory of their adaptability to acid or alkaline reaction, according to their respective constitution.

Phenolphthalein, a weak acid, reacts red by dissociation in presence of a strong alkali; in presence of ammonia and alcohol the reaction may be restrained and again developed by addition of water. Methyl orange, cyanine, and corralline were similarly demonstrated.

A letter was read from the general secretary stating that "at the closing session of the midwinter meeting at Columbia University, December 28, by unanimous vote, the cordial thanks of the Society were extended to the New York Section for the bountiful hospitalities of the section, which were so heartily enjoyed by the members of the society during the eighteenth general meeting.

DURAND WOODMAN, *Secretary.*

The February meeting was held in the Assembly Room of the Chemists' Club, 108 West 55th Street, Friday evening, the 10th, Dr. William McMurtrie in the chair.

The secretary being absent, Mr. Seldner was appointed secretary, *pro tem.*

A communication from the Washington Section was read in reference to conferring with the Chemical Society of London, as to the feasibility of the separate publication of their abstracts after the manner of the *Chemisches Centralblatt*, the preparation of which should be undertaken by both societies conjointly.

The section voted in favor of the project.

A report of the Committee on Patent Legislation recommended continuation of the present committee and its increase from five to ten members, the additional members to be appointed by the chair. Dr. Smith moved acceptance of the report and adoption of its recommendations. The motion was carried.

Papers were read as follows:

"Recent Extension of Our Knowledge Regarding Nitrates as Plant Food," by J. A. Myers.

"Method for the Analysis of Canned Condensed Milk," by Frederick S. Hyde.

"Manufacture of Ether," by Alfred Roos.

"Manufacture of a New Guaiacol Compound," by Ludwig H. Reuter.

"Explosibility of Nitrogen Iodide and Acetylene Copper Compounds and the Use of the Latter for the Manufacture of Alcohol and Ether," by Ludwig H. Reuter.

"Chemistry of the Dynamite Process of Weighting Silk," by Rafael Granja.

"The Chemistry of the Velocitan Process—Quick Tanning," by Rafael Granja.

"Melting-Point as a Cyclic Function," by Thomas Bayley, England. Read by title.

Abstract from minutes of R. Seldner, Secretary *pro. tem.*

DURAND WOODMAN, *Secretary.*

NORTH EASTERN SECTION.

The regular monthly meeting of the North Eastern Section was held February 17th at the Exchange Club, Boston. About fifty members were in attendance. The secretary's report was read and approved. A letter was read from the secretary of the Washington Section asking for action on a resolution adopted by that section. In accordance with this request the question was placed before the section and it was unanimously voted to recommend to the council to provide for a conference with the Chemical Society of London as to the feasibility of the separate publication of their abstracts after the manner of the *Chemisches Centralblatt*, the preparation of these abstracts to be undertaken by both societies conjointly.

The president then introduced Mr. Clifford Richardson of the Barber Asphalt Paving Co., who presented an interesting and comprehensive address on asphalt. The speaker described the various sources of asphalt, the peculiar geological formations connected with them, and gave particular attention to the Trinidad asphalt lake, describing experiments made to ascertain its depth, composition, rapidity of inflow, and the like. The chemical composition of the bitumen was also considered in some detail. A lengthy discussion followed the paper, and a vote of thanks was extended to the speaker.

Professor H. P. Talbot then presented a criticism of Carnot's "Traite d'Analyse," a new work on analytical chemistry, to consist, when complete, of three volumes of a thousand pages each.

Professor L. P. Kinnicutt called the attention of the members to a new form of compound blowpipe of neat design. He also described the form of apparatus devised by Dr. G. W. Fitz, of Harvard College, to be used for the determination of carbon dioxide in the air. The simplicity of the apparatus and of its manipulation makes it available for the use of inexperienced persons. According to the work of some of Professor Kinnicutt's students, the accuracy of the results obtained with it leave little to be desired.

Mr. A. D. Little exhibited two samples of artificial silk, one made from nitrocellulose and the other from ordinary glue treated with formaldehyde. The processes of manufacture were also described. Mr. Little also presented some samples of photographic dyeing of cotton cloth. The cloth was sensitized with a bichromate solution, was exposed in the usual way beneath a negative, and the prints were developed by the use of various organic dyes.

After the adjournment of the meeting an informal lunch was served.

W. R. WHITNEY, *Secretary*.

Issued with April Number, 1899.

Proceedings.

BOARD OF DIRECTORS.

MINUTES OF THE MEETING OF THE BOARD OF DIRECTORS OF THE AMERICAN CHEMICAL SOCIETY.

The meeting was held in the Chemists' Club, 108 W. 55th St., New York City, Friday evening, March 10, 1899. The meeting was called to order at 7.40 P. M., by President Morley. The directors present were Messrs. Morley, Chandler, Hale, McMurtrie, and Doremus. The secretary read a telegram from Dr. Charles B. Dudley, director, regretting his inability to be present, on account of the illness of two of his assistants.

Minutes of previous meetings were approved as recorded. The following resolutions were adopted:

1. *Resolved*, That Albert C. Hale, secretary, and Charles F. McKenna, treasurer, and their successors in office, shall have the right of access to the safe (No. 13,580) in the vaults of the Mercantile Safe Deposit Company, standing in the name of this society.

2. *Resolved*, That the secretary of the society be directed to move that the motion of Dr. Hillebrand with reference to the question of appointing a committee to communicate with the Chemical Society of London in regard to the matter of publishing abstracts, be referred to the Committee on Abstracts and Reviews which was appointed by the directors at their meeting held October 7, 1897; that this Committee be increased to five members by appointment by the president of the society; and that said Committee be instructed to investigate the matter mentioned in Dr. Hillebrand's motion, and to report to the council as promptly as possible.

3. *Resolved*, That bids for printing and binding 3,000 copies of the index of the first twenty volumes of the Journal, prepared by Mr. M. D. Sohon, be obtained by the secretary of the society, and that he be authorized to let the work to the lowest bidder who will give sufficient assurance that it will be done satisfactorily, in uniform style with the printing and binding of the Journal.

Resolved, further, that a copy of the index be furnished to each member of the society, if desired, for fifty cents ($0.50), and that the price of the index to non-members be fixed at seventy-five cents ($0.75) per copy.

4. *Resolved*, That the sum of two hundred dollars ($200) be, and the same is hereby appropriated and payable to the treasurer of the society for the expenses of his office during the year 1899.

5. *Resolved*, That the investment of the sum of one thousand, one hundred and sixteen dollars and ninety-eight cents ($1,116.98) in purchasing a $1,000 New York City 3½ per cent. gold bond, at 110½ and accrued interest, for the benefit of the Life Membership Fund, as made by the treasurer after consultation with the Finance Committee and those of the directors who were accessible, be and the same is hereby authorized and approved by the board of directors.

6. *Resolved*, That in accordance with the request of the treasurer, Charles F. McKenna, his accounts and his management of the funds of the society during the whole period of his service as treasurer be examined and audited by the Finance Committee of the society.

After a brief statement of the present condition of the treasury by Mr. McKenna, the meeting was adjourned.

ALBERT C. HALE, *Secretary*.

COUNCIL.

The council has voted that the next meeting be held at Columbus, Ohio, August 21 and 22, 1899, in connection with the session of section C of the American Association for the Advancement of Science.

The following officers have been elected by the council for the term specified :

Albert C. Hale, secretary, for the year 1899.

Edward Hart, editor, for the year 1899.

Charles F. McKenna, treasurer, for the year 1899.

Marston Taylor Bogert, librarian, for the year 1899.

Charles B. Dudley and Charles A. Doremus, directors, for two years beginning January 1, 1899.

Charles A. Doremus, A. A. Breneman, and Peter T. Austen, Committee on Membership, for the year 1899.

A. H. Sabin, A. P. Hallock, and Elwyn Waller, Committee on Finance, for the year 1899.

NAMES PROPOSED FOR MEMBERSHIP.

Bigelow, Henry W., care Pope Mfg. Co., Hartford, Conn.
Cady, Walter B., Agr. Expt. Sta., Columbia, Mo.
Campbell, Archibald, 639 So. 12th St., Ann Arbor, Mich.
Du Vivier, Ernest H., 22 Warren St., N. Y. City.
Divine, Robert E., 75 Niagara St., Buffalo, N. Y.
Fetterman, John C., Western Univ. of Pa., Allegheny, Pa.
Goddard, Henry N., Oshkosh, Wis.
Haywood, W. G., State Chemist's Office, Raleigh, N. C.
Humphrey, Richard L., City Hall, Philadelphia, Pa.
Jones, Frederick W., Barwick Rd., Ware, Herts, England.
Lawson, Thomas W., care Baltimore Copper Sm. & Ref. Co., Keyser Bldg., Baltimore, Md.
Levine, Edmund J., 340 W. 88th St., N. Y. City.
Lihme, C. B., care Ill. Zinc Co., Peru, Ill.
Morton, Cora, Main Ave., Norwood, Hamilton Co., O.
Ritchey, J. C., 506 Washington St., Steubenville, O.
Roberts, W. H., City Hall, Minneapolis, Minn.
Snyder, Oscar, J., Room 23, Y. M. C. A. Bldg., Minneapolis, Minn.
Stevens, Alviso B., 915 Oakland Ave., Ann Arbor, Mich.
Weissmann, 221 Molitor St., Cincinnati, O.
Wetterstroem, Theodore D., Spring Grove Ave. and Copper St., Cincinnati, O.

NAME PROPOSED FOR ASSOCIATE MEMBERSHIP.

Goldstein, Harris, 15 Montgomery St., Manhattan, N. Y. City.

NEW MEMBERS ELECTED MARCH 2, 1899.

Aylsworth, J. W., 165 Cleveland St., Orange, N. J.
Baxter, William T., 47 St. Felix St., Brooklyn, N. Y.
Banghart, Edgar D., Wymore, Nebr.
Bradbury, Robert Hart, Central M. T. School, Philadelphia.
Brewster, Edward E., 316 East C St., Iron Mountain, Mich.
Hamilton, H. C., 637 Baker St., Detroit, Mich.
Hardenburgh, Louis M., Iron Mountain, Mich.
Hazard, F. R., Solvay Process Co., Syracuse, N. Y.
Horton, E. G., Lab. State Board of Health, Columbus, O.
Kendall, Robert Everett, 96 Warren St., Glens Falls, N. Y.
Koch, Charles F., 2334 Ashland Ave., Cincinnati, O.
Lamar, William Robinson, 55 W. 127th St., N. Y. City.
Lamborn, Leebert L., care Curtis Davis & Co., 136 State St., Boston, Mass.
Lee, Waldemar, 2802 W. Lehigh Ave., Philadelphia, Pa.
Linton, J. H., 3012 Wabash Ave., Chicago, Ill.
McCay, Leroy Wiley, Princeton, N. J.

Neiman, Howard S., 8 E. 97th St., N. Y. City.
Porter, Arthur F., 143 Lexington Ave., N. Y. City.
Rippetoe, J. J., Vallejo, Cal.
Rogers, Allen, Univ. of Maine, Orono, Me.
Schober, W. B., Lehigh Univ., South Bethlehem, Pa.
Spieler, Augustus J., Syracuse, N. Y.
Street, John Phillips, New Brunswick, N. J.
Wiener, William, 62½ Nelson Place, Newark, N. J.
Wilkens, H. A. J., care N. J. Zinc Co., 52 Wall St., N. Y. City.
Witherspoon, Thomas A., 27 Iowa Circle, Washington, D. C.

ASSOCIATES ELECTED MARCH 2, 1899.

Cayvan, Llewellyn L., 660 Sixth Street, South Boston, Mass.
Driehaus, Irwin W., Madisonville, O.
Fetsch, William, 2530 W. 6th St., Cincinnati, O.
Hildreth, Edward T., 87 University Road, Brookline, Mass.
Ripley, Philip F., Andover, Mass.
Russell, George F., care Russell Paper Co., Lawrence, Mass.
Young, Charlotte S., Mt. Hope Road, Price Hill, Cincinnati, Ohio.

CHANGES OF ADDRESS.

Austen, Peter T., 52 Beaver St., N. Y. City.
Axtell, Frank C., Box 116, Short Hills, N. J.
Aylsworth, J. W., 223 Midland Ave., East Orange, N. J.
Culmann, Julius, Barrett House, Engle St., Englewood, N. J.
De Benneville, James S., University Club, 1510 Walnut St., Philadelphia, Pa.
Lustig, A. L., Care Lexington Print Works, Canton, Mass.
Mallory, J. Halsey, Care Georgia Cotton Oil Co., 409 Fitten Bldg., Atlanta, Georgia.
Miller, P. Schuyler, Mt. Prospect Lab., Flatbush Ave., Brooklyn, N. Y.
Wilder, S. W., Jr., 13 Pearl St., Boston, Mass.

MEETINGS OF THE SECTIONS.

WASHINGTON SECTION.

The regular meeting of the Washington Section was held on February 9, 1899.

The first paper of the evening was read by Mr. F. D. Simons, and was entitled, "The Detection of Caramel Coloring-matter in Spirits and Vinegar," by C. A. Crampton and F. D. Simons.

"The paper states that the two principal tests given in the books for the detection of caramel coloring-matter are, first, the reduction of Fehling's solution, and second, the precipitation of the caramel by means of paraldehyde. Neither of these tests has given satisfactory results in the hands of the authors.

"It was found that fuller's earth had a selective affinity for caramel coloring-matter in spirits, while the natural color derived from wood was but slightly affected. The test is made by beating up twenty-five grams of the earth with fifty cc. of the sample to be tested, allowing it to stand thirty minutes at room temperature, and filtering. The color before and after treatment is observed by Lovibond's tintometer or other good form of colorimeter, and the amount of color removed ascertained in this way.

"The test was applied to all the samples of spirits available in the Laboratory of Internal Revenue, positive results being obtained in all cases. A series of forty samples known to be naturally colored, gave an average of 14.6 per cent. of color removed, while eighteen samples of the spirits known to be colored with caramel averaged 44.7 per cent. of color removed. The test was also applied to a few samples of vinegar with good results."

The second paper of the evening was read by Dr. David T. Day, and was entitled "Characteristics of Iridosmium in the United States."

"A demand has lately arisen for this material as a source of osmium, with which it is proposed to impregnate the filaments of incandescent lights with most beneficial results, as to the amount of light supplied by a given current and the increased life of the lamp. The problem of supplying a large amount of osmiridium is a most fascinating one and has led to much study in the localities of the West where platinum metals have been found. The results show that platinum is much more generally distributed through the western placer mines than was supposed and that there are many localities containing so-called crude platinum, in which osmiridium is found. A sample sent from the Oregon beach contained as high as ninety-nine per cent. of osmiridium. The Hay Fork District, in Trinity County, California, Junction City, and more especially the whole Pacific Coast beach is a most interesting field of search, because the platinum is mixed with much osmiridium. It can be said in general that nearly all the crude platinum sand contains osmiridium in greater or less quantity, according to the analyses of a great number of samples made by Dr. Waldron Shapleigh for the Welsbach Light Company. An interesting exception is the Granite Creek district in British Columbia. A curious form of osmiridium was noted at the Chapman Mine, near Junction City, California, where nuggets one-half inch in diameter, when treated with warm dilute aqua regia, yield platinum in solution, and flakes of osmiridium. The separation of the platinum from osmiridium is readily accomplished by means of aqua regia and the separation of osmic acid from the residue is quite simple by the ordinary process of passing chlorine over the osmiridium mixed with salt. The purification of the osmic acid is now effected by redistillation, but it is probable that these methods will be much improved in the next few months. It is probable that 2,000 ounces of the material will be obtained during 1899."

The last paper of the evening was read by Dr. Day, and was entitled "Uses of Fuller's Earth as a Filtering Medium."

"In 1892 an effort was made by the Owl Cigar Manufacturing Company, at Quincy, Florida, to manufacture brick from a peculiar cream-colored clay found on their property. Instead of baking hard, it exfoliated in a peculiar manner and caused some comment from an Alsatian cigar-maker in the employ of the company, who noticed this clay and called attention to its close resemblance to German fuller's earth. This led to an inquiry as to its value as fuller's earth, at a time when the lubricating oil companies were looking for domestic fuller's earth, to replace animal charcoal as a means of lightening the color of lubricating oils by filtration. The earth proved very suitable and its use extended in this direction as well as to some extent to the bleaching of vegetable oils. But for the latter purpose the imported fuller's earth is still approved. The number of samples of clays which have been called fuller's earth and sent to the consumers for examination since that date, is almost beyond belief. It has been shown that fuller's earth is quite widely scattered in the northwestern counties of Florida and the adjacent counties of Georgia.

"In the latter region the fact that it grades into chalcedony makes it more probable that the fuller's earth is a chemical precipitate and this is further indicated by the replacement of calcium carbonate by the silica in many shells found associated with the fuller's earth.

"The Florida and English fuller's earths differ greatly in appearance and to some extent in chemical composition. English fuller's earth has found its analogue in the material discovered at Fairburn, near Rapid City, South Dakota, and Valentine, Nebraska. It is altogether probable that further developments will make the material from these places an important article for use in bleaching cottonseed oil. There is an interesting difference in the method of testing the Florida fuller's earth as compared with the English. It is the constant practice of the lubricating oil companies to simply fill large slightly conical cylinders with the fuller's earth, ground to about forty mesh, through which the oil is filtered at about a temperature equal to that of boiling water. At first the filtrate is perfectly colorless and, strange to say, lighter in specific gravity and more fluid than the unfiltered oil, a fact which will probably be made use of in chemical separations of the future. I am now using this in investigating oils. Fuller's earth is used for bleaching refined golden cottonseed oil to a light straw color. When the resultant oil is to be used for white products, such as lard substitutes, the fuller's earth is ground to a fine powder and stirred into the oil slightly above the temperature of boiling water. After a thorough mixing by agitation for a few moments the bleached oil is simply filtered through bag presses. Perhaps the most interesting feature of this use of fuller's earth is the very slight difference in the two varieties of fuller's earth in regard to their bleaching capacity, which leads to their acceptance or rejection. Little regard is paid to chemical analysis, but the tests made by filtration on a small scale are most severe."

WILLIAM H. KRUG, *Secretary.*

CINCINNATI SECTION.

The sixty-sixth regular meeting of the section was held on Wednesday, February 15th, in the Chemical Lecture Room of Hanna Hall, University Buildings, with twenty-one members present, and President Simonson in the chair.

Prof. T. H. Norton gave some additional information regarding the occurrence of the diamond in Wisconsin, in continuation of his paper read at the December meeting on this subject. Dr. William Groff then made a brief but interesting report on some curious phenomena observable at some of the Egyptian pyramids, notably the will-o'-the-wisp, a phenomenon that has given rise to much superstitious interpretation by the inhabitants of that region. The possible origin of this phenomenon was the subject of some discussion. Prof. George Jackson then read a short paper on the discovery of radium, a new element, and on the occurrence of hydrogen in the atmosphere as a regular constituent. Prof. John Uri Lloyd finally gave some interesting notes on the early history of salicylic acid in the United States. In this connection he called attention to a peculiar reaction which takes place between salicylic acid and borax, resulting, under certain conditions, in the formation of an exceedingly bitter compound. This reaction was observed by Prof. Lloyd and others many years ago, and was studied in detail by E. Jahns in 1878.[1]

S. WALDBOTT, *Secretary.*

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[1] *Arch. d. Pharm.*, 212, 212.

NEW YORK SECTION.

The regular monthly meeting of the New York Section of the American Chemical Society was held on Friday evening, the 10th inst., at the Chemists' Club, 108 West Fifty-fifth street, Dr. Wm. McMurtrie presiding and eighty-five members present. Dr. Doremus made a special announcement of the annual exhibition of the New York Academy of Sciences, and urged any members having new and interesting material to contribute the same to the exhibits.

The following papers were then read:

(1) "Preparation of Graphitoidal Silicium," by Frederick S. Hyde.

(2) "The Conservation of Energy in the Human Body," by W. O. Atwater.

(3) "Paraffin as an Adulterant of Oleomargarine," by Joseph F. Geisler.

(4) "Manufacture of Pure Phenyldimethylpyrazolonsulphonic Acid," by L. H. Reuter.

(5) "Manufacture of β-Naphthalenesulphonic Acid and Benzoylsulphonic Acid for the Manufacture of Ether," by L. H. Reuter.

(6) "On the Determination of Sulphur in Sulphites," by A. Bourgougnon.

While the first paper was before the meeting, the president of the society, Prof. E. W. Morley, of Cleveland, arrived, and was invited to take the chair. He made a few remarks on the interest taken in the section by its members, as evidenced not only by the full attendance and interesting list of papers to be read at this meeting, but by the uniformly high character and abundance of material announced for each and every meeting.

Prof. Atwater stated that the large calorimeter chamber in which a man can live for a week or more at a time, has been so perfected that an analysis of pure alcohol by combustion can be made in it to within one-tenth per cent. of the theoretical composition. The results on the calorific value of foods as consumed in the human body, agree very closely with the results calculated from experiments with the bomb calorimeter. The chief difficulties at present are in regard to certain constants, as for instance the value of the calorie, the latent heat of evaporation of water at different temperatures, etc. The calculation of the observations from a week's run of the calorimeter chamber is itself an arduous and exacting piece of work. Thus far the law of the conservation of energy in the human body is fully demonstrated, within a very small error, which it is hoped to eliminate entirely.

J. F. Geisler exhibited a sample of paraffin extracted from adulterated butter, which contained about forty-five grains of the wax per ounce.

Butter samples had been purchased in New York and vicinity containing from 5 to 11.75 per cent. paraffin.

DURAND WOODMAN, *Secretary.*

NORTH CAROLINA SECTION—ANNUAL MEETING, FEB. 11, 1899.

The fourth annual meeting was held in the office of the state chemist in Raleigh, beginning at 11.30 o'clock, A.M. Thirteen members were present. Reports were read from the Committee on Membership, and from the delegates to the first and second conventions of the National Pure Food and Drug Congress.

A communication was read from the general secretary informing the section that its request as to headquarters and territory were approved by the society. The section decided to approve the recommendation of the Washington Section requesting publishers to make announcements of new books on library cards of standard size. The section decided to join with the Washington Section in recommending to the society the publication of abstracts jointly with the Chemical Society of London. The secretary was authorized and instructed to have printed the announcement of the section for 1899.

The following officers were elected for the ensuing year :

President: Dr. Charles Baskerville, University of N. C., Chapel Hill.

Vice-President: Prof. Charles E. Brewer, Wake Forest College, Wake Forest.

Secretary and Treasurer: Mr. Charles B. Williams, Assistant State Chemist, Raleigh.

Member of Council for 1900: Prof. W. A. Withers, A. and M. College, Raleigh.

The following papers were read :

1. President's Address: "The Nature of Valence," by Dr. F. P. Venable.

2. "An Observation on Free and Albuminoid Ammonia in Drinking Water," by Prof. A. W. Blair.

3. "On the Occurrence of Chromium and Titanium in Peats from the Dismal Swamp," by Dr. Charles Baskerville.

4. "Iron and Aluminium Phosphates in Commercial Fertilizers," by Mr. Charles B. Williams.

5. "The Action of Sodium Malonic Methyl Ester on Dichloroxalic Methyl Ester," by Dr. Thomas Clarke.

6. "Food Adulteration in North Carolina," by Prof. W. A. Withers.

7. "Some Organic Salts of Zirconium," by Dr. F. P. Venable.

8. "A New Burette Holder," by Dr. J. M. Pickel.

9. "The Condensation of Chloral with Ortho-, Para-, and Metanitraniline," by Dr. Charles Baskerville.

10. "A Preliminary Report on Secondary Heptylamine," by Dr. Thomas Clarke.

11. "A Case of Spontaneous Combustion," by Dr. Charles Baskerville.

W. A. WITHERS, *Secretary*.

RHODE ISLAND SECTION.

The regular monthly meeting of the Rhode Island Section of the American Chemical Society was held at the Hope Club, Providence, January 26, 1899, at eight o'clock, with Mr. Edward D. Pearce as presiding officer.

After dinner, Mr. Walter M. Saunders presented the paper of the meeting on "Alloys." His remarks were supplemented by lantern-slides, showing phenomena connected with the dissolving of one metal in another, and the subsequent crystallizing when cooled.

Attention was called to the fact that varying proportions of common salt and water change materially the solidifying-point of the mixture. On a chart it was shown that the freezing-point of the mixture is lowered until a so-called eutectic alloy is obtained, when the point again is higher, according to the proportions. From analogy the same is observed in certain mixtures of metals.

The regular monthly meeting of the Rhode Island Section of the American Chemical Society was held at the Hope Club, Providence, February 23, 1899, at eight o'clock, with Mr. Edward D. Pearce as presiding officer.

After dinner, the members and guests went to the Chemical Laboratory of Brown University. Dr. E. A. Fourneaux presented the paper of the evening on "The Process of Mercerizing."

When cotton cloth or yarn is immersed in a strong solution of caustic soda for a few seconds, washed and stretched, the condition of the fiber is greatly changed in appearance and in its conduct towards dye-stuffs. Dr. Fourneaux was able to show by experiments, performed before his audience, how samples of the same kind of cloth dyed with a common material but treated differently in mercerizing, may vary in finish and shade. If the cloth is printed with substances which protect the fibers in the process of mercerizing and then dyed, a figure may appear on the surface, caused by the difference in shade between the parts mercerized and dyed, and the parts unmercerized and dyed.

WALTER E. SMITH, *Secretary.*

CORRESPONDENCE.

To the Editor of the Journal:

MY DEAR PROFESSOR HART: In connection with the minutes of the meeting of the Board of Directors enclosed herewith, I would like to call the attention of the members of the society especially to the investment which has just been made for a permanent "Life Membership Fund," and also to the fact that this has been promptly followed by the payment of a life membership fee of $100, just received from Professor Charles E. Munroe. Doubtless there are others who will be glad to avail themselves of the opportunity of becoming life members or life associates, when they know that the policy of the society is now definitely fixed to maintain a permanent fund, separately invested, covering all life membership fees which the society has ever received, or which shall hereafter be paid; and that this fund will be administered in accordance with the following provisions of the Constitution:

"Article I, Section 6. Any member or associate, not in arrears, paying at any one time the sum of one hundred dollars into the treasury of the society, as commutation for dues, shall become a life member or life associate, shall be exempt from the further payment of annual dues, and shall receive all the regular publications of the society."

"Article X, Section 2. All funds received for life membership shall be invested as soon as possible and shall constitute a trust fund to be known as the 'Life Membership Fund,' which shall be held in perpetuity to guarantee the future interests of such life members. The interest of such fund not required for the above-named purposes shall be set aside as a 'Research Fund,' from which appropriations may be made annually by the council, but only for the purposes of chemical research."

Yours very truly,

ALBERT C. HALE,

Secretary of the American Chemical Society.

Issued with May Number, 1899.

Proceedings.

COUNCIL.

The Council has authorized the establishment of a section to be known as the Philadelphia Section, with headquarters in Philadelphia, Pa., and with a territory with a radius of sixty miles from the Philadelphia City Hall where this does not conflict with the territory of any existing section.

NAMES PROPOSED FOR MEMBERSHIP.

Austin, Ned M., Leechburg, Pa.
Bancroft, Wilder D., 7 East Ave., Ithaca, N. Y.
Brown, Herman E., Coldwater, Mich.
Carel, Herbert C., Dept. of Med., Univ. of Minn., Minneapolis, Minn.
Chace, Edward M., Berwyn, Md.
Clements, Frank O., Westerville, Ohio.
Cook, Charles G., Boys' High School, Brooklyn, N. Y.
Faust, John K., Carpenter Steel Co., Reading, Pa.
Folsom, Herbert A., Atlantic Mills, Olneyville, R. I.
Foster, John, Woodward, Ala.
Hinckley, J. Fred., care B. T. Babbitt & Co., N. Y. City.
Lloyd, George, 52 Dearborn St., Chicago, Ill.
Longstaff, J. P., Chem. Lab., Univ. of Edinburgh, Scotland.
Loos, Edward A., 933 N. Front St., Philadelphia.
McDowell, Alexander H., 457 W. 21st St., N. Y. City.
Motion, John, care John Ellis & Co., Edgewater, N. J.
Nelson, N., Ill. Steel Co., South Chicago, Ill.
Nichols, Herbert T., Springs Junction, Arizona.
Primrose, H. W., Exp. Station, Raleigh, N. C.
Pullman, F. Cooper, Carpenter Steel Co., Reading, Pa.
Van Brunt, Charles G., Augustine, Kas.
Ware, Ezra J., 221 Baldwin Ave., Detroit, Mich.
Worden, Edward C., 103 W. 42nd St., N. Y. City.

NAMES PROPOSED FOR ASSOCIATE MEMBERSHIP.

Ashley, Harrison E., 6 Rutland Square, Boston, Mass.
Darke, Jesse M., Gen. Elec. Steel Foundry Co., West Lynn, Mass.

Knight, Geo. W., 38 Rosseter St., Boston, Mass.
Powell, Thomas H., 53 S. Main St., South Norwalk, Conn.
Skinner, Hervey J., 15 Chestnut St., Wakefield, Mass.
Summey, Albert E., 46 Main St., Bradford, Pa.
Teasdale, Wm. S., The Teasdale Dye House, Race St., Cincinnati, Ohio.

CHANGES OF ADDRESS.

Arnold, Fred. N., Jr., 117 Huffman Ave., Dayton, Ohio.
Austen, Peter T., 218 St. Johns Place, Brooklyn, N. Y.
Best, Otto, Daggett, Cal.
Briggs, T. Lynton, Box 533, Ridgewood, N. J.
Cottle, George T., 39 Curtis Ave., Wallingford, Conn.
Gies, William J., 437 W. 59th St., New York City.
Hall, Arthur W., care Ziegler Electric Co., 141 Franklin St., Boston, Mass.
Hanna, Prof. Geo. B., Box 26, Charlotte, N. C.
Hicks, Edwin F., 203 W. 81st St., New York City.
Jones, Clemens C., 908 W. Franklin St., Richmond, Va.
Kelley, J. H., 321 N. Vine St., Nashville, Tenn.
LaBach, J. O., Pleasant Ridge, Hamilton Co., Ohio.
Lerch, Fred., Hibbing, Minn.
Ludlow, Gabriel, The Commercial Guano Co., Savannah, Ga.
Maury, G. P., Mount Iron, St. Louis Co., Minn.
Nelson, E. K., 159 E. 47th St., Chicago, Ill.
Poole, Herman, 357 Canal St., N. Y. City.
Quinan, W. R., Wellington, South Africa.
Roller, H. C., Roselle, N. J.
Saltar, J. C., Pemberton, N. J.
Schweitzer, Hugo, 427 W. 117th St., N. Y. City.
Seamon, W. H., Box 97, El Paso, Texas.
Smith, Horace T., 137 E. Main St., Bridgeport, Conn.
Takamine, Jokichi, 475 Central Park, West, New York City.
Thatcher, Charles, 132 Columbia Heights, Brooklyn, N.Y.
Van Ingen, Dudley A., care N. J. Zinc Co., Newark, N. J.
Wakeman, Alfred J., Greenwich, Conn.
Wigfall, E. Newton, Box 257, Somerville, N. J.
Wolcott, James T., 255 Ellicott St., Buffalo, N. Y.

MEETINGS OF THE SECTIONS.

CHICAGO SECTION.

The February meeting of the Chicago Section was held at the Technical Club on Thursday, the 28th. The program consisted of a paper by Wm. Hoskins "On the Chlorination of Gold

Ores." This was followed by a general discussion of the subject.

At the 27th regular meeting of the Chicago Section held at the Technical Club, March 29th, Mr. Clement W. Andrews, Librarian of the John Crerar Library, gave a paper on "Some Proposed Recent and Proposed Scientific Bibliographical Work." Prof. W. D. Bancroft, of Cornell University, then gave an informal talk on the relation between physical chemistry and technical chemistry.

F. B. DAINS, *Secretary*.

COLUMBUS SECTION.

Since the last report, the following papers have been read and discussed before the Columbus Section.

1. "The Summer Meeting of the American Association for the Advancement of Science," by Prof. H. A. Weber.

2. "Technical Analysis" by Prof. N. W. Lord.

The speaker discussed "Short Methods" in chemical analysis and called attention to the danger of devoting too much time to teaching them at the expense of the training of students in chemical science, thus giving a sort of "cook-book" knowledge of chemical processes; the student is thus left poorly prepared to meet the demand for wide-awake chemists ready for whatever may come to them in the rapidly increasing range of analytical necessities.

3. "Essential Oils" by Prof. G. B. Kauffman.

The subject was considered under two heads:

a. Natural oils—their source, preparation, and properties.

b. Artificial oils—their preparation, properties, and relation to the corresponding natural oils. In some cases, as oil of wintergreen, the two are identical, while in others they simply possess similar properties.

Attention was called to the frequent use of the artificial for the natural products and of the difficulty which the physician and pharmacist experience in distinguishing between the two. Even in the case of oil of wintergreen, there is still a demand for the natural product.

4. "Drug-Using and Drug-Proving," by Prof. C. A. Dye.

The speaker discussed the distinction usually made between empirical and rational therapeutics, and gave a general outline of the methods employed for scientific drug-proving, including the experiments on the lower forms of life, and the application of the knowledge thus obtained to the treatment of diseases.

5. "The Winter Meeting of the American Chemical Society," by Prof. W. A. Henderson.

The following officers have been elected for the ensuing year:

President—H. A. Weber.

Secretary—William McPherson.

Treasurer—O. R. Flynn.

Executive Committee—H. A. Weber, Wm. McPherson, and O. R. Flynn.

Member of Council—N. W. Lord.

Committee on Membership—Geo. B. Kauffman. A. M. Bleile, and N. W. Lord.

The section has accepted an invitation from the Cincinnati Section for a joint meeting to be held on the evening of April 15th.

The following are the abstracts of the papers presented at the regular monthly meeting held April 5, 1899.

Mr. Foulk gave a short account of his experience with the solubility of platinum in fused sodium carbonate. When an iron ore is fused and subsequently titrated with bichromate after reduction with stannous chloride, the complication introduced by the presence of small amounts of platinum is very troublesome and may lead to a serious error in the result.

A direct experiment showed that in one hour 14.3 milligrams of platinum were dissolved from forty-four cm. surface exposed.

Mr. Foulk referred to the absence of any reference in the text-books to this solubility of platinum and gave the few statements in the periodical literature which he had been able to find. Under the ordinary conditions of a fusion, from one-half to one milligram of platinum was dissolved from the crucible. This agreed with the experiments of Dr. Koenick and Mahon which were referred to.

Mr. Peppel read a short paper giving the results of some experiments on the stability of sodium thiosulphate solutions. The conflicting statements of the text-books and of the periodical literature were first referred to and then the results of a series of laboratory experiments were given.

Various methods were used in preparing the thiosulphate but in only one case—when the recrystallized salt had been washed in ether and alcohol—was a product obtained, the calculated weight of which could be used in preparing standard solutions. By using ordinary care in making up the solutions, Mr. Peppel found them to remain constant for four months which was the time the experiments had been going in. No extra precautions were taken in keeping the thiosulphate. Solutions were contained in clear glass bottles and in no way protected from the light.

Mr. Vinson discussed the "Mechanical Separation of Butter-fat from Milk." The Alpha separator which was used in his experiments was explained by means of charts. The milk separated from the butter-fat by this machine showed the presence of 0.01 per cent. butter-fat according to the Babcock tester. Careful analyses made by the Adams method, using sufficient paper to absorb fifteen grams of the milk, gave 0.11 per cent. butter-fat. The separators used in the University Dairy School recover ninety-eight per cent. of the butter-fat. Some observations were also given on the melting-point of butter-fat from pasteurized milk, which subject the author will carefully investigate.

WILLIAM MCPHERSON, *Secretary.*

CINCINNATI SECTION.

The sixty-seventh regular meeting of the section took place on Wednesday, March 15th, in the Chemical Lecture Room of Hanna Hall, University Buildings, and was the occasion of a joint meeting with the Cincinnati Academy of Pharmacy. Twenty-three members were in attendance, President Simonson in the chair.

A resolution adopted by the Washington Section having been received and communicated at the previons meeting, with reference to the feasibility of suggesting to the London Chemical Society, through appropriate channels, the separate publication of their "Abstracts" under the auspices of the London and the American Chemical Societies, conjointly, was unanimously endorsed at this meeting.

Prof. John Uri Lloyd read a paper, entitled "An Investigation into 'Husa,' an Asserted Plant Preparation to Cure the Opium Habit."

Prof. Lloyd was able to secure authentic specimens of the preparation consisting of ten numbered bottles, each containing about ninety cc. of a uniformly brown liquid. According to a printed label they bear, the collection represents the amount to be used in the first month's treatment. The cost of this supply is ten dollars. A preliminary analysis of the contents of one of the bottles brought to light the following ingredients: Morphine 1.3 per cent. (approximately), present as sulphate; salicylic acid, 0.16 per cent.; alcohol, 12 per cent.; glycerol 10 per cent., and coloring-matter, probably burnt sugar.

A subsequent assay of each of the ten specimens for morphine showed that the quantity of morphine present gradually decreased from 2.19 per cent. to 1.33 per cent. The morphine obtained conformed to all the tests of the U. S. Pharmacopœia, and in addition, to Mayer's alkaloidal test as well as to the iodic acid test.

A prolonged discussion followed the reading of the paper.

Upon motion, the meeting adjourned.

S. WALDBOTT, *Secretary.*

NEW YORK SECTION.

The regular monthly meeting of the New York Section of the American Chemical Society was held at the Chemists' Club, 108 West Fifty-fifth Street, on Friday evening, April 7th, Dr. Wm. McMurtrie presiding, and about sixty-five members present.

The following papers were read : "The Toxic Action of Sodium Fluoride," by H. B. Baldwin. "The Chemistry of the By-products of Coke Ovens," by J. D. Pennock. "Notes on the Chemistry of the Carbides," by J. A. Matthews. "The Distribution of Alkali in Montana," by F. W. Traphagen and W. M. Cobleigh ; read by Mr. Cobleigh.

DURAND WOODMAN, *Secretary.*

CORRESPONDENCE.

UNITED STATES COMMISSION TO THE PARIS EXPOSITION OF 1900.

CHICAGO OFFICES, April 4, 1899.

GENTLEMEN :

For the benefit of the trade which you represent will you please state that all who desire to exhibit in the Paris Exposition of 1900 are requested to immediately notify this office, if they have not already done so, in order that they may be considered in the allotment of space which will soon be made. While there are many applications on file in every line of industry, it is desirable that the American Sections be not only representative of this country but also represent the largest possible number of producers. Both our commercial interests and national pride demand that our works be entered in this most important International Exposition. It is estimated that fully 60,000,000 people from every part of the globe will attend, and it will be an opportunity to greatly increase our foreign trade and to demonstrate that the United States is supreme in tne arts of peace.*** Respectfully,

JOHN H. MCGIBBONS,
Director of Exploitation.

Approved, FERDINAND W. PECK,
Commissioner-General.

Issued with June Number, 1899.

Proceedings.

COUNCIL.

The resignation of Charles F. McKenna was accepted by the Council, April 28, 1899, the Council adopting the following resolutions:

"*Resolved*, That the Council of the American Chemical Society, in accepting the resignation of Dr. Charles F. McKenna, Treasurer, takes such action with very deep regret, and only upon the urgent representation by Dr. McKenna that the demands of his private business prevent any consideration of his continuing to perform the duties of said office.

"*Resolved*, Further, that the Council, in behalf of the Society, herewith expresses to Dr. McKenna its high appreciation of his long-continued, faithful, and laborious services as Treasurer, and its sincere thanks for the efficient administration of the duties of his office. It is a matter of special gratification to the officers and members that the financial affairs of the Society are to-day in better condition than ever before, and the Council takes pleasure in recording that this result is very largely due to the wise, conservative business management of the retiring Treasurer."

At the same time Albert P. Hallock was elected Treasurer of the Society.

On May 9, the Council adopted the following resolutions:

(1) *Resolved*, That the resignation of Mr. Marston Taylor Bogert as Librarian of the American Chemical Society be accepted, and that the thanks of the Society be hereby tendered to Mr. Bogert, through the Council, for his efficient services in that office.

(2) *Resolved*, That Professor A. A. Breneman be, and is hereby, authorized and employed to serve as Acting Librarian of the American Chemical Society until a permanent librarian shall be elected.

The Librarian has been authorized to have an edition of 300 copies of the Journal for January, 1899, printed by the Chemical Publishing Company at $1.05 per page, according to the bid submitted by said Company.

The section adopted the third Thursday of each month, except July and August, for stated meetings of the section.

D. W. Harding read a paper on the "Derivatives of the Atomic Mass of Palladium."

F. E. DODGE, *Secretary.*

RHODE ISLAND SECTION.

The regular monthly meeting of the Rhode Island Section of the American Chemical Society was held at the Hope Club, Providence, April 27, 1899, with Mr. Edward D. Pearce as presiding officer.

After dinner, Mr. Charles A. Catlin of the Rumford Chemical Company, presented a paper on "Culinary Phosphates."

The reader referred briefly to the history of cooking, laying particular stress upon the early appreciation of the dietetic value of a light cellular structure in bread, with a very general reference to various ways and means adopted for its attainment, citing as one of the most efficient, the aeration of the dough through the evolution within it of carbon dioxide by chemical reaction between an alkaline bicarbonate and an acid or acid salt, and calling attention to the fact that it was as an agent in this latter operation that culinary phosphates play their part. The history of the culinary application of the phosphates is interesting. The peculiar behavior of phosphoric acid and its salts had been most perplexing. Graham's classic research in 1833 furnished a clearer conception of these and roused great interest in their study. Liebig pushing on in his brilliant career found them everywhere associated with life, and finally proved them essential to life of every form. Horsford, the pupil and assistant of Liebig, caught the inspiration of the master and finally his inventive genius suggested the employment of, in place of the questionable acids and acid salts used in connection with sodium bicarbonate as leavening agents, acid phosphate of calcium. It was many years however before careful research enabled him to present the article, under the name of cream of tartar substitute, in any reasonable commercial condition because of its extremely acid and deliquescent character. Finally the discovery of a process for the manufacture of monocalcic phosphate preparations without the deliquescent free phosphoric acid has so improved it that it has made a place for itself *per se* no longer as a substitute but standing by itself alone, now known as "phosphate acid." The reader called attention to the undesirable qualities of preparations of this kind wherein free phosphoric acid present induces too rapid evolution of the gas of the bicarbonate when mixed therewith in use, as well as to the deliquescent property of such compound prohibiting their safe employment in baking-powders; gave methods also for the determination of these qualities exactly, calling attention to the uncertainties of estimations of value based wholly upon the titration with caustic alkali solutions, never having found in his experience of twenty-six years and the examination of many thousand samples, a single case wherein the equivalent sodium bicarbonate as shown by the titration process could be made to evolve its entire carbon dioxide under the conditions of the baking process, despite statements to the contrary based evidently upon purely theoretical considerations. Attention was called to the use of normal phosphoric acid solutions in indirect titration of such compounds. Attention was also called to the secondary reaction of monocalcic phosphate with sodium bicarbonate in presence of artificial hydrated calcium sulphate and showing its value in certain baking operations which, however, unrecognized by food inspectors is sometimes condemned as adulteration of terra alba. Manufacturers of monocalcic salts are often put to great expense and trouble to remove from their goods this incidental impurity which really in some kinds of baking work may be a valuable assistant.

Baking-powders in which monocalcic phosphate preparations are used, could formerly be presented commercially only in tightly sealed bottles; now, by reason of great advances, the manufacture of a monocalcic phosphate preparation without deliquescent properties has been attained, and the goods are sold in ordinary unsealed cans; these improved goods have perfect commercial stability.

The reader then gave methods for determining the relative commercial stability of baking-powders: Having determined in each the carbon dioxide content, weighed samples of the powders to be compared are exposed to the humid atmospheric influence obtained by suspending them over water under a bell glass, and the carbon dioxide determined in each after the same length of exposure, relative loss under same conditions and during exactly the same periods of time indicating relative stability. Attention was called to the fact that, not alone the amount of available carbon dioxide, but the conditions under which it was evolved, determined the leavening value of a baking-powder, and gave methods for the determination of these.

Finally particular attention was called to the usefulness of determination of the gravimetric density taken in connection with available carbon dioxide content in the valuation of a baking-powder. Domestic use of baking-powders is always by measure, never by weight. Experience has proved that the most efficient work in ordinary practice of cooking is obtained from a baking-powder capable of yielding about fifty times its volume of available gas; very much more, or very much less than this in the ordinary cook's practice, yields poor results. Methods of arriving at a measure of the volumes of baking-powders and apparatus employed, were described. The most reliable commercial gravimetric density is that obtained through the volume of the powder as purchased in the can and the weight of the same. Other standards, such as per cent. by weight of available gas, for instance, are liable to be misleading.

WALTER E. SMITH, *Secretary*.

CHICAGO SECTION.

The 28th meeting of the Chicago Section was held at the Technical Club, Friday, April 28th, 1899.

Dr. J. H. Long gave a brief talk on "Oils," after which the section adjourned to the convenient laboratory of the Dearborn Drug and Chemical Co., 29 Rialto Building, where Mr. W. A. Converse described the physical testing of oils illustrating by a number of practical tests.

Prof. H. W. Wiley, of Washington, while in Chicago as an expert in the Pure Food Investigation, was given a dinner by the local section at the Technical Club, May 10, 1899. After the dinner, the members had the pleasure of listening to informal addresses from Prof. Wiley and from Mr. Wm. McMurtrie of the New York Section, who was also the guest of the club.

F. B. DAINS, *Secretary*.